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RADIATION CHEMISTRY AND CABLE TECHNOLOGY

E. E. Finkel, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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RADIATION CHEMISTRY AND CABLE TECHNOLOGY

by

E. E. Finkel', S. S. Leshchenko
R. P. Braginskiy



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The scientific and technical principles of the radiation modification of electrical insulating polymeric materials used in electrotechnical (mainly in cable), radio engineering, and the electronic industry are presented. An analysis is made of the physicochemical bases for the use of ionizing radiations for the modification of properties of polymers, the essence of radiochemical processes flowing in them during irradiation, and the peculiarities of action of radiation of various forms. Fundamental information on the radiation chemistry of polymeric systems is given and a detailed examination is made of the characteristics of radiation-modified electrical insulating polymeric materials under specific operating conditions.

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R. P. Braginskiy

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

RADIATION CHEMISTRY AND CABLE TECHNOLOGY

E. E. Finkel', S. S. Leshchenko, and
R. P. Braginskiy.

Moscow 1968

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In the book the scientific and technical principles of the radiation modification of electrical insulating polymeric materials used in electrotechnical (mainly in cable), radio engineering, and the electronic industry are presented. An analysis is made of the physicochemical basis for the use of ionizing radiations for the modification of properties of polymers, the essence of radiochemical processes following in them during irradiation, and the peculiarities of action of radiation of various forms. Fundamental information is given on the radiation chemistry of polymeric systems (the mechanisms of radiochemical reactions, the change in the chemical structure of polymers during irradiation, the influence of the conditions of irradiation, phase state, and features of the structure of the polymer, the influence of additions, etc.). A detailed examination is made of the characteristics of radiation-modified electrical insulating polymeric materials under specific operating conditions (elevated temperatures, mechanical overloadings, radiation fields, the conditions of space) and the most worthwhile fields of

their application are revealed. Along with the analysis of the radiation stability of polymeric electrical insulating materials the possibilities are examined of a directed change in their properties with the help of irradiation. The practical application of the methods of radiation modification of polymers is confirmed by data on the increase in heat resistance and the reliability of irradiated cable products for various application. A brief account is given of the engineering bases for radiation technology relative to cable technology and some technical-economical evaluations are given. Bibliography - 565 Titles. Illustrations - 54. Tables - 45.

PREFACE

In recent years in radiation chemistry in general as well as in radiation chemistry of polymers in particular a tendency was determined for the transition from the conducting of searches and research work to the relization of technical radiation processes.

Today a number of radiochemical processes, among other things the process of radiation modification of electrical insulating polymeric materisls, are in the stage of research-and-development assimilation. In connection with this in this book in a form which is accessible for the specialists of various profile the bases have been presented for the radiation chemistry of polymers and the study of radiation materials, and also the principles of radiation modification, including the elements of technical-engineering solutions.

In the Soviet Union and abroad a number of momographs have been published which deal with the effect of radiation on polymeric materials (F. Bovey, "The Influence of Ionizing Radiations on Natural and Synthetic Polymers," 1959; T. S. Nikitina, et. al., "The Influence of Ionizing Radiations of Polymers," 1959; A. Charlesby, "Nuclear Radiations and Polymers," 1962; A. Svollou, "Radiation Chemistry of Organic Compounds," 1963;

R. Bolt, and J. Kerrol, "The Influence of Radiation on Organic Materials," 1965; I. V. Vereshchinskiy, A. I. Pikayev, "Introduction to Radiation Chemistry," 1965, and others). However, in these books applied questions either are not examined at all or have been treated in too general a view.

In order to make up this ommission at least partly, literature on the characteristics of cable products with radiation modified insulation, the fields of application and also their behavior under specific operating conditions (in radiation fields, space, and others) have been systematized.

Although primary attention here is allotted to applied problems, all the available publications through 1966 inclusively have also been examined.

The mastering of the specific technology on industrial scales and the consumption of production obtained by radiation methods in various branches of the national economy is impossible without acquainting a wide circle of specialists with the specifics of radiation processes and the possibilities opened during their utilization.

It is possible to hope that the proposed work will facilitate the more rapid and wider incorporation of radiochemical methods in the national economy.

INTRODUCTION

During the entire history of humanity the discovery of every previously unknown form of energy signified by itself the beginning of a new considerable stage in science and technology and was accompanied by intensive investigations and by engineering development, the purpose of which was the practical utilization of this form of energy. The discovery of atomic energy is no exception from the general regularity.

In spite of the fact that the processes themselves of intranuclear transformations, which are accompanied by the liberation of energy exceeding the energy which is liberated by chemical reactions, were discovered already at the end of the last century it became possible to use atomic energy in practice only after the discovery of the fission reaction of the nuclei of heavy elements (for instance, uranium) under the action of neutrons. Precisely this discovery, made at the end of the thirties, predetermined the possibility of the realization of a controlled chain reaction of the fission of an atomic nucleus, which was realized for the first time on 2 December 1942, when the first nuclear reactor, installed under the guidance of the outstanding Italian physicist Enrico Fermi, began to operate.

As a result of the division the nucleus of a heavy element decomposes into two identically charged fragments which diverge at

very high speeds. During the collision of these fragments with the atoms of the atmosphere in which they are moving the kinetic energy of the latter is converted into thermal. The quantity of energy liberated in this process exceeds by more than 10' times the energy content which is liberated during the radioactive decay of atomic nuclei. During the complete nuclear fission of 1 kg of uranium energy is liberated which is equivalent to the heat of combustion of about 3000 t of high-calorific anthracite. The essential feature of the fission reaction consists of the fact that during every fission for one absorbed neutron two and more neutrons are liberated, i.e., the reaction bears a chain nature. From the total energy which is liberated during the realization of the chain reaction of the fission of heavy nuclei about 80% of it is converted into thermal, and the remaining 20% is liberated in the form of ionizing high-energy radiation. The ionizing radiations generated in a nuclear reactor can be used either directly or for obtaining various radioactive isotopes; the latter can also be liberated in large quantities from fission products.

Thus as a result of conducting a controlled chain reaction of the division of the nuclei of heavy elements colossal quantity of heat energy is liberated, intensive flows of the ionizing radiations of high energy are generated, and radioactive isotopes are obtained. At the present time as a result of the large number of the works executed by scientists, engineers, and other specialists, promising trends have been revealed and paths have been found for the utilization of nuclear energy, radiations, and isotopes in industry, agriculture, medicine, and scientific investigations.

Thus, for instance, the radioactive isotopes which are formed in a nuclear reactor found wide application as "tracer elements" for investigations in the most diverse branches of science and engineering, medicine, and agriculture (research on the mechanism of chemical reactions, diffusion and self-diffusion;

study on the wear of tools and parts, the assimilation of fertilizers by plants; the diagnostics of a number of illnesses; radiotherapy; the study of the migration of agricultural pests, etc.). Along with use for research purposes the radioactive isotopes of a number of elements are used in significant quantities for the creation of small electric power installations (with a power up to 100 W) in which the energy liberated during radioactive decay is converted into electrical. Such current generators find use as the power packs for ground (radio beacons, weather bases, seismic stations set up in almost inaccessible places, etc.) and also for space equipment (satellites, interplanetary probes). Finally radioactive isotopes are used for the creation of the powerful radiation sources used in radiochemical processes, for the sterilization of medical equipment and materials, for the extermination of insects on grain, preservation of food products, etc. Recently there has been wide discussion on the possibilities of chemionuclear synthesis, i.e., the conducting of radiochemical reactions directly in the nuclear reactor core under the influence of fission fragments.

There is no less value in the use of isotopes in measuring technology, especially, for the creation of devices for the checking and control of different industrial processes. The characteristic properties of radioisotope sets are noncontact measurement, low degree of inertness, high-performance, and stability. Level gauges, tachometers, sensors of small movements and vibrations, thickness gauges, pipe-thickness gage, desiometers, manometers, gas flowmeters, hygrometers for solid and loose materials, etc., with radioisotope sensors are being produced.

Even the far from complete enumeration of the fields of application of radioactive isotopes and radiations gives an idea about how widely disseminated atomic technology is in the different fields of human activity. However, as it was noted, for isotopes and radiation only about 20% of the energy which is liberated in the nuclear reactor is expended; the remaining 80% is

converted into heat. The most worthwhile method of the utilization of heat energy is its conversion into electrical, i.e., the creation of atomic electric power stations (AES) [АЭС].

With an electric power of reactors of 600-1000 thousand KW the atomic power stations become competitive in relationship to the contemporary thermal power plants of analogous power. Apparently in the Soviet Union, in regions with expensive fuel, nuclear power engineering after 1980 will become one of the fundamental development trends of power engineering.

The development of atomic technology in all its diversity of uses, and especially the development of nuclear power engineering and the building of the powerful isotope radiation sources, substantially influenced the electrical insulating and cables industry.

Actually cable products, for example, fulfill a double function. On the one hand they serve for the delivery of electric power supply to various sets and equipment which enter the system for control and protection of a nuclear reactor or isotope radiation source; on the other hand, over them information is transmitted from different sensors to the system of automatic regulation or to the desk of operator and the subsequent transmission of instructions to final mechanism. In both cases cable products, at least a certain part of them are laid out in the zone of influence of ionizing radiations.

Sometimes the specifics of utilization of cable and other electrotechnical products in reactors or isotope installations are not limited only to the presence of the flows of ionizing high-energy radiation, they are characterized by the combination of irradiation with the action of considerable temperatures. In a number of cases in addition to the two factors there are others, for example, the periodic raising in humidity, fluctuation of temperature over wide limits, etc., which still further complicate

the operating conditions. The use of nuclear powerplants aboard man-made satellites or spaceships introduces into the features enumerated above of the operating conditions near a radiation source all the specifics of space - high vacuum, ultraviolet and corpuscular radiation, etc.

As a result it is necessary to develop cable products on the basis of materials which are suitable for prolonged exploitation under very complex conditions which are specific for the uses in question. It is evident that such a development should precede the selection of materials not only on the basis of an analysis of their electrophysical, physicomechanical, and technical properties, but also taking into account the changes in the majority of these properties during irradiation under certain conditions. In other words the determining factor becomes the radiation stability of the material. The inclusion of this factor in the examination during the analysis of the fitness of electrical insulating materials used in cable technology for exploitation under such specific conditions substantially narrowed their nomenclature and stimulated searches, and sometimes also the development of new materials which correspond to the more complex, as compared with usual, requirements. The study of the properties of materials which were not being used in cable technology, the design elaboration of cable products with the use of such materials, and the creation of the technology of their preparation made it possible not only to solve the concrete problems in the field of atomic technology, but also to rise cable technology to a new stage, having enriched its possibilities in respect both to the assortment of utilized materials and the arsenal of technical methods and means.

Thus the introduction of concepts and methods of radiation material study into the custom of specialists in the field of electrical insulating and cable technology is a natural refelction of the development of contemporary science and technology, it simulates the further perfection of cable technology relative to

the demands not only of atomic industry, but also other rapidly developing branches of the national economy.

On the other hand, precisely the development of nuclear power engineering and reactor engineering required the conducting of the systematic studies in the field of radiation materials behavior, i.e., the study of the processes which proceed in various materials under the influence of ionizing high-energy radiation, and also the changes in the properties of materials during irradiation. The data obtained during the conducting of such studies showed that in certain cases ionizing radiations can be used as a unique instrument for a directed change in the properties of initial materials. The irradiation of some materials by ionizing radiations under specific conditions makes it possible to change the properties of the initial material in the required direction, i.e., to modify the material without introducing into its composition any supplementary ingredients. As it was explained, the methods of radiation modification in the first place are applicable to electrical insulating materials on the basis of synthetic polymers. Thus the perfection of atomic technology and the obtaining of powerful sources of the ionizing radiations opened supplementary possibilities in cable technology, it permitted the creating of new electrical insulating materials with improved properties by means of the radiation modification of the generally used synthetic high polymers.

The presence of such an interrelation between atomic and cable technology is completely regular and its realization facilitates the more rapid and fruitful development of these branches of knowledge.

For the realization of methods of the radiation modification of materials on industrial scales it is possible, and in certain cases even more advantageous, along with a nuclear reactor of an isotope source to use an electron accelerator as the generator

of radiation. Under conditions of industrial production for processes which require the significant irradiation dose at a high dose rate, the bundle of accelerated electrons has explicit advantages over the gamma-irradiation of an isotope source. The scales of utilization of accelerators for industrial purposes are noticeably increasing. Thus based on data for 1966 of the 1800 accelerators which have been built and are operating in more than 40 countries of the world, more than 100 accelerators are used in industry; in the USA alone for the conducting of one of the most developed and promising of radiochemical processes - the cross-linking of polyethylene and other polyolefins into products (wires and cables, packing film, insulation tubes, etc.) - 36 accelerators are used.

The prospect of the use of the methods of radiation modification for increasing the heat resistance and reliability of polyolefin insulation of wires and cables is confirmed by the systematic growth in the production of such products abroad, especially, in the USA, and also by the utilization of such irradiated insulation in cable products of ever greater nomenclature (wiring leads, coaxial cables, power and high-voltage cables, etc.). Thus today wires and cables with insulation from irradiated polyethylene and its copolymers are produced by the following firms: "Raychem. Corp," "General Electric Co.," "Electronized Chemicals Corp.," "Radiation Materials Inc.," "Anaconda Wire and Cable Co.," "Supernant," "Radiation Dynamics Inc.," and others, whereupon, according to the Atomic Energy Commission of the USA, the total volume of production in 1963 in terms of money was 13 million dollars, in 1964 - 27, in 1965 - 40, and in 1966 70 million dollars was planned.

The radiation chemistry of polymers and its practical use in various aspects obtained wide development in our country. A number of radiochemical processes have already been brought to the stage of industrial testing, and an even greater number is found on the threshold of this stage.

In the next two or three years radiochemical processes will be introduced intensively into industrial production. Therefore, it is important that the specifics of radiation technology and the possibilities appearing during its wide utilization would be equally clear to the workers in the branches of industry which master the output of radiation-modified products and which use them.

The purpose of this work is to acquaint a wide circle of technical-engineering personnel, in the first place of the electrotechnical and radio engineering industry and their consumers, with the basic concepts of the radiation chemistry of polymers and radiation materials behavior and the systematization of the necessary minimum of information for independent work with original literature, and also the reflection in an accessible form of the contemporary level of development of the industrial use of radiochemical processes for the modification of electrical insulating polymeric materials.

CHAPTER I

THE PHYSICOCHEMICAL BASES FOR THE USE OF IONIZING RADIATIONS FOR THE MODIFICATION OF PROPERTIES OF ELECTRICAL INSULATING POLYMERIC MATERIALS

FORMS OF IONIZING RADIATIONS, METHODS OF GENERATING THEM, AND PECULIARITIES OF THE INTERACTION WITH A SUBSTANCE

The terms "ionizing radiations" and "high-energy radiation" are applied both to corpuscular radiation, i.e., to particles moving at high velocity - to fast electrons or β-particles, to rapid protons, neutrons[1], deutons, and α-particles, and to short-wave electromagnetic radiation - X-ray and γ-rays; the latter can be considered as particle flux (quanta of high energy).

Let us examine the nature and properties of ionizing radiations, the methods of obtaining them, and also the peculiarities of interaction with a substance.

[1]Strictly speaking, neutrons do not directly cause the ionization of the atmosphere in which they are disseminated, however, they make a noticeable contribution to ionization as a result of secondary effects.

The Interaction of Fast-moving Charged Particles with a Substance

A charged high-energy particle spends its kinetic energy as a result of the electric (Coulomb) interaction with the bound electrons of the atoms of the absorbing material (the absorber). This interaction gives rise to the direct transmission of energy to such electrons and to their transition into the excitation levels of the corresponding atoms or molecules. If these levels lie higher than the ionization potential of the given atom (or molecule), then ionization occurs; if they are arranged lower than the ionization potential (in a bound state), then an exicted atom (or molecule) is formed. Since the dimensions of the nucleus are considerably less than the dimensions of the atom, and the action of nuclear forces is manifested only at very small distances, the power loss by an incident particle as a result of collision with nuclei is less probable than as a result of an interaction with electrons.

When a charged particle passes near a bound electron the magnitude of the energy transmitted to it depends on the particle velocity and minimum distance at which it approaches the electron (the so-called "impact parameter"). The Coulomb force of the interaction between the incident particle and electron is proportional to the product of the charges of the interacting particles divided by the square of the distance between them. The magnitude of the pulse transmitted to the electron is determined by the product of this force and the duration of interaction, i.e., is inversely proportional to the velocity of the incident particle.

If the velocity of motion of the particle is less than the orbital velocity of the electron in the atom of the absorber, then it can capture this electron from the atom. During the further passage of this particle through the substance of absorber

the electron captured by it can again be stripped, or charge transfer (charge-exchange) can occur between the atom of the absorber and particle.

The power loss by the charged particle with mass M (greater than the mass of the electron) per unit of path length for ionization and the excitation of the atoms of the absorber for the nonrelativistic[1] range can be expressed by formula [1]

$$-\frac{dE}{dx} = \frac{4\pi e^4 (ez)^2 ZN}{mv^2} B, \qquad (1)$$

where E - the kinetic energy of the particle; x - the path length of a particle with mass M in absorber; e - the electron charge; ez - the charge of the incident particle; N - the number of atoms in 1 cm^3 of absorber substance; Z - the atomic number of the absorber substance; m - the mass of the electron; v - the particle velocity; B - the slowing-down coefficient. The slowing-down coefficient B is a logarithmic function of v and Z[2]. Therefore the dependence of dE/dx on the particle velocity is determined basically by the multiplier $1/v^2$. Logarithmic function B weakly influences the dependence of the losses of energies on the atomic number of the absorber. Therefore in the case of constant velocity the magnitude dE, dx is practically proportional to the

---

[1] i.e., when the velocity of the incident particle is considerably less than the speed of light.

[2] The slowing-down coefficient B can be calculated according to the formula

$$B = \left[\ln \frac{2mv^2}{I} - \ln (1-\beta^2) - \beta^2\right] Z,$$

where I - the average excitation potential of the substance of the absorber; $\beta = \frac{v}{c}$ (c - the speed of light in a void).

For nonrelativistic energies (at $\beta = 0$) the expression for B is simplified:

$$B = Z \ln \frac{2mv^2}{I}.$$

product of NZ, i.e., the electron density of the absorber.

The kinetic energy of the particle diminishes to the level of thermal (~0.025 eV) after the passage of a determined thickness of material which is called the particle path: the magnitude of the path is frequently expressed in units of surface density (mg/cm^2).

Electrons

The electron is a negatively charged particle. The rest mass of an electron comprises 1/1837 the rest mass of a proton; the electron possesses a charge of 4.803×10^{-10} esu. The positron possesses exactly the same mass as the electron, but has a positive charge; it can be considered as an antielectron[2].

Depending on the nature of the process leading to the appearance of a free electron, it is possible to introduce the following classification.

β-*particles* are electrons of the high energy which are formed during radioactive decay; the electron in this case is emitted by the atomic nucleus. The energy spectrum of β-particles emitted during radioactive decay is continuous: from zero to the certain peak value of energy, characteristic precisely for the given form of decomposing nuclei (so called the upper bound of the β-spectrum of the given radioactive isotope). The mean energy of a β-particle comprises about 1/3 from the maximum energy of electrons emitted in the decay of the given radioactive isotope.

The *cathose rays* are electrons emitted by a heated metallic filament (the cathode); they can be accelerated to any required energy. Actually all high-energy electrons obtained with the help of special electrophysical devices - accelerators, are cathode rays, however this term is usually used only relative to electrons of relatively low energy.

Compton electrons are formed during the interaction of γ- or x-rays with the atomic electrons of the absorber. The energy of Compton electrons is changed over wide limits: beginning from zero and ending with an energy almost equal to the incident radiant energy.

δ-rays are secondary electrons which are formed within the limits of the track of the ionizing particle and which receive from it a certain fraction of energy; their zone of action is localized near the particle track. The energy of δ-rays fluctuates over wide limits: from several electron volts to a maximum which can be transmitted by an incident particle to an electron with the observance of the laws of conservation of energy and pulse.

Photoelectrons are formed during the interaction of the x-rays or γ-quanta of low energy with the bound electrons of the atoms of the absorber as a result of photoelectric absorption (photo-effect). The kinetic energy of a photoelectron is equal to the total energy of its dislodged x-radiation or γ-quantum with the deduction of the binding energy of the electron in the atom at that level from which it was removed.

The electrons of internal conversion are formed during interaction of γ-quantum emitted by nucleus in the act of radioactive transformation with the electron of one of the electron shells (K-, Z- or M-shells adjacent to the nucleus of the same atom.

The physical aspects of the interaction of electrons with a substance are reduced to the following.

Electrons of not very high energies (several magaelectronvolts) spend their energy up to complete deceleration, basically as a result of manifold successive inelastic collisions with the atomic electrons of the absorber.

During inelastic interactions in the case of the collision of incident electrons with the orbital electrons of the atom the energy is expended for excitation and ionization of the atoms of the substance (ionization losses), and during their abrupt deceleration in the Coulomb field of the nucleus - for the generation of slowing-down x-radiation (radiation losses). The ionization losses of energy of electrons are described by a somewhat modified equation (1) for the loss of energy for ionization and excitation.

The difference in the behavior of electrons and of heavier charged particles lies in the following. A heavy particle (see below) during every collision with an electron loses a comparatively small part of its kinetic energy and as a result it does not substantially change the direction if its movement, i.e., its path in the substance is practically a straight line. If the incident particle is the electron, then it is considerably deflected from the original direction of movement and its path in the absorber is very meandering.

Radiation losses (the emission of "braking radiation") make up a significant portion of the total energy losses when the velocity of electrons is close to the speed of light. The relationship of radiation and ionization losses can be described approximately by the equation

$$\frac{\left(-\frac{dE}{dx}\right)_{\text{radiation}}}{\left(-\frac{dE}{dx}\right)_{\text{ionization}}} \approx \frac{EZ}{800}, \qquad (2)$$

where E - the energy of the electron, MeV; Z - the atomic number of the absorbing substance.

Radiation losses are higher, the higher the energy of the electrons and the greater the atomic number of the absorber. For instance, during the braking of electrons with an energy of 15 MeV in carbon (Z = 6) radiation losses make up 10% of ionization losses.

The heavy ionizing high energy particles are obtained mainly with the help of special physical devices - the accelerators of charged particles, with the exception of α-particles which are emitted during the radioactive decay of the atomic nuclei of some heavy elements which possess natural radioactivity.

The physical properties of heavy ionizing particles are given in Table 1; there for a comparison the properties of a neutron and of light particles (electron and positron) are given.

Table 1. The physical properties of ionizing particles.

Particle	Symbol	Rest mass (amu)[1]	Charge in units of electron charge
Proton	p or H^+	1.00728	1
Deuton	d or D^+	2.01355	1
α-particle Helium ion	α He^{2+}	4.00047	2
Neutron	n	1.00867	0
Electron	e^-	$5.486 \cdot 10^{-4}$	1
Positron	e^+	$5.486 \cdot 10^{-4}$	1

[1] One (amu) (atomic mass unit) is equal to 1/12 the atomic mass of the isotope of carbon C^{12}.

The general regularities of the absorption of charged particles in a substance are described in the beginning of this section. As can be seen from expression (1), the loss rate of energy by positive ions does not depend on the mass of the particle, but it is determined only by its velocity and charge. With equal velocities of movement in a substance the loss rate of energy by the helium ions (Z = 2) is four times greater than by protons (Z = 1). The ionization density generated by a heavy particle in the substance along the length of track is irregular and

increases up to its ends, which is conditioned by the loss of velocity.

During the irradiation of a substance by heavy charged particles, as in the case of electrons, δ-rays are also formed, i.e., secondary electrons; the majority of the events of ionization and excitation in the absorber is caused namely by δ-rays. Maximum energy of δ-rays, i.e., of secondary electrons with mass m which are formed under the action of heavy particles with mass M and energy E, is determined by the relationship

$$E_{t,\max} = 4E\frac{mM}{(m+M)^2} \approx \frac{4Em}{M}. \qquad (3)$$

Since the maximum energy of δ-rays is inversely proportional to the mass of the ionizing particle, the heavier particles give rise to the formation of more compact and more intensive tracks.

Neutrons

Neutrons are distinguished from the other forms of high-energy radiation in the first place by the absence of an electric charge; neutrons do not interact electrically with electrons and atomic nuclei. Not being ionizing particles in a literal sense, neutrons transmit energy to the surrounding substance mainly by means of elastic collisions with the atomic nuclei of the absorber. Ionization and excitation in the substance during irradiation by high-energy neutrons are caused by charged recoil particles.

A free neutron possesses radioactivity; having suffered β-decay, it is converted into a proton, whereupon the half-life comprises 11.7 min [2, 3].

Depending on energy (also for convenience being expressed in electron volts) neutrons are subdivided into several groups.

Such a classification is quite conditional and with various authors does not always coincide.

Thermal neutrons. This group includes neutrons, the mean kinetic energy of which coincides with the kinetic energy of particles with a mass of 1 (amu) at room temperature (i.e., about 0.025 eV and velocity on the order of 2200 m/s).

Epithermal neutrons. This group includes neutrons, the energy of which is higher than the energy of thermal neutrons but lower than intermediate. In this area of energies many elements possess high values of effective cross section of resonance capture.

Intermediate neutrons. This group includes neutrons, the energy of which lies in the range of approximately 100 eV up to 100 keV. The recoil protons created by such neutrons barely form secondary ionizing particles (threshold energy for formation of δ-rays by protons comprises about 20 keV).

Fast neutrons. This group includes neutrons with an energy above 100 keV.

The number of neutrons which intersect a given cross-sectional area in a unit of time is called the "neutron flux." If in the system in question there is on the average n neutrons per 1 cm^3, whereupon each of them possesses the velocity v (cm/s), then the neutron flux comprises nv [neutron/($cm^2 \cdot s$)]. The total number of neutrons which are necessary for every square centimeter of the irradiated surface of the system i.e., the integral of neutron irradiation, is obtained by means of the multiplication of the neutron flux by the duration of irradiation: nvt (neutrons/cm^2)

Neutrons are not encountered in a free state in nature and their only source are nuclear reactions. The most powerful

neutron source is the nuclear reactor. The neutron flux and its energy spectrum depend on the type and dimension of the reactor, and also on the level of power at which it works. Furthermore, in different sections within the limits of the given reactor the flux is different.

The classical neutron source is a radium-beryllium source, in which neutrons are formed during the nuclear bombardment of beryllium by α-particles of radium in the reaction

$$_4Be^9 + {}_2\alpha \rightarrow {}_6C^{12} + {}_0n^1$$

or as it has been accepted to write down briefly $Be^9(\alpha, n)C^{12}$.

The neutron source can also be an accelerator of charged particles. The neutron yield in this case depends on the energy of the particles which bombard the target and the form of the nuclear reaction which flows in it. Thus a convenient source of rapid neutrons can be the nuclear reaction $H^2(d, n)He^3$. The beam of deutons, accelerated with the help of Van de Graff electrostatic generator (see below), is directed to a target in the form of ice from heavy water D_2O. When using ions D^+ with an energy of 1 MeV the neutron yield comprises about $5 \cdot 10^9$ *neutron/s* per 1 μA. of deutron current. By means of the irradiation of a beryllium target by an electron beam with an energy above 2 MeV it is possible to carry out the nuclear reaction $Be^9(\gamma, n)Be^8$ or $D^2(\gamma, n)H^1$.

Unlike charged particles and γ-quanta, neutrons in transit through a substance interact mainly only with the atomic nuclei; electrons hardly participate in this process. Not having an electric charge, a neutron can approach atomic nuclei at distances which are sufficient for the development of nuclear forces without possessing high kinetic energy in this case, because it does not experience repulsion on the part of the Coulomb field of the nucleus. During the interaction of neutrons with a substance four fundamental processes take place: elastic and

inelastic scattering, radiation capture, the emission of charged particles, and the nuclear fission of heavy elements.

During elastic scattering the kinetic energy of neutrons will be redistributed between impinging neutrons and nuclei with which the suffer collision; with this the energy will be redistributed in accordance with the laws of classical mechanics - inversely proportional to the masses of the colliding particles. Thus during the collision of a neutron which possesses energy E with a nucleus which has mass M the recoil energy E_r can be changed from zero to the peak value determined by the equation

$$E_{r.\max} = \frac{4M}{(M+1)^2} E. \qquad (4)$$

The average energy of recoil comprises approximately half the maximum energy; for instance, during neutron scattering by protons (M = 1) the average energy of the recoil protons is equal to half the energy of impinging neutrons.

During inelastic scattering part of the kinetic energy of the neutron is spent on the excitation of the nucleus, therefore the neutron in such a process loses more energy than during elastic scattering.

Both the examined processes of interaction are characteristic mainly for rapid and partly for intermediate neutrons. As a result of the manifold consecutively flowing scatterings in the substance the neutrons are slowed down.

In order to describe the process of the interaction of neutrons with a substance, they introduce the value of the effective cross section of the nuclear reaction σ, being expressed either in square centimeters or in barns (1 barn = 10^{-24} cm^2) - the method of expressing the probability of the course of the given reaction. The numerical value of magnitude σ as a rule does

not agree with the geometric cross section of the nucleus (calculated on the basis of the known radius) and can be both considerably less and much more than it.

When a neutron collides with a nucleus and is implanted in it a compound nucleus is formed. If such a process flows with the participation of the thermal neutron, then in most cases the excitation energy of the compound nucleus is too low for the emission of a charged particle; therefore nucleus passes over from excited state into fundamental by means of de-excitation of γ-quanta. On this foundation such a process is called "radiation capture."

For thermal and epithermal neutrons the probability of the process of radiation capture is determined by the specific properties of the nucleus. In general the value of σ is inversely proportional to the velocity of the neutron: $\sigma \sim \frac{1}{v}\left(\sim \frac{1}{\sqrt{E}}\right)$. Such a relationship is conditioned by the fact that the duration of stay of the neutron near nucleus, which determines the probability of an interaction, is proportional to 1/v. However, if the neutron energy somewhat exceeds thermal, then another process called "resonance capture" becomes more probable. In the range of neutron energy 0.1-1000 eV the dependence of the magnitude σ of radiation capture on the neutron energy E for many elements has a clearly expressed maximum. The physical sense of this phenomenon consists of the following: if the energy of excitation of the compound nucleus which is formed from the bombarded nucleus and neutron is equal to the energy of one of its quantum quasi-stationary states, then reaction cross section of the neutrons which possess precisely this energy increases a thousand times.

The nucleus can capture a fast neutron and emit a charged particle. Reactions of this type are characterized by a specific energy threshold of neutrons (specifically it can be equal to zero). With an energy which exceeds threshold, σ reactions practically do not depend on the neutron energy. For the emission

of a positively charged particle (proton, deuton, or α-particle) from the nucleus it is necessary that it possess sufficient energy for overcoming the binding energy in the nucleus and passage through the potential Coulomb barrier.

The nuclei of some heavy elements (U^{235}, U^{233}, PU^{239}) during the capture of a neutron and the formation of an excited compound nucleus do not return to the ground state with the emission of γ-quanta or a charged particle, but decompose into two fragments with the emission of several excess neutrons (the process of division). Since the values of the relationship of the content of neutrons and protons in both fragments are obtained somewhat higher than mean values for stable nuclei, many fission products prove to be radioactive. During successive radioactive transformations these fragments pass over into a stable state. γ-quanta are emitted both during division and during the radioactive decay of the fission products formed.

Electromagnetic Radiations

The electromagnetic radiations which are of interest during the study of radiation effects in a substance include γ- and x-rays and bremsstrahlung radiation.

γ-radiation emerges during intranulcear processes, for example, during the radioactive decay of an excited nucleus after neutron capture. Such γ-radiation is monoenergetic, although some nuclei can emit γ-quanta, and not from one, but from several levels (the nucleus of Co^{60} for every event of γ-decay emits two γ-quanta with energies of 1.17 and 1.33 MeV).

Roentgen rays are formed during the interaction of charged high energy particles with a substance. They appear as a result of two effects. The first effect consists of the destruction of the atom of the target by an incident electron, whereupon the

atomic electron is dislodged from the shell adjacent to the nucleus. With the filling of this shell with electrons from adjacent shells arranged further from nucleus x-radiation is emitted. These x-rays have a discrete spectrum which corresponds to the energies of transition between electronic levels in the atom of the irradiated element. The second effect - the loss of energy by electrons during slowing down in the Coulomb field of the nucleus - gives rise to the generation of bremsstrahlung which is characterized by a uninterrupted energy spectrum.

A number of sources of electromagnetic radiation exist. The simplest is the x-ray tube which works over a range of voltages of 50-200 kV. High flows of bremsstrahlung when using adequate targets can be obtained in electron accelerators (electrostatic generators, betatrons, and others). As sources of γ-radiation they frequently use the radioactive isotopes Co^{60} (half-life 5.3 years) and Cs^{137} (half-life 30 years), which emit γ-quanta with energies of 1.25 MeV (average) and 0.66 MeV respectively, and also the spent fuel elements [tvely] (твэлы) from reactors with a large neutron flux. Finally a γ-source of high intensity is the radiation circuit of a nuclear reactor.[1]

The process of absorption of electromagnetic radiation has its characteristic properties. In contrast to charged particles electromagnetic radiation does not have a specific path length in a substance. The charged particles spend their energy during manifold successive collisions, i.e., in small portions; electromagnetic radiation, independent of the mechanism of interaction with the atmosphere, is absorbed in one event and is finally lead out from the beam which is disseminated in the substance, or it is scattered and changes direction of movement, whereupon its energy diminishes (incoherent scattering). This means that the number of γ-quanta, absorbed in a layer of substance with a

[1]Sources of the ionizing radiations are examined in more detail in Chapter V.

thickness dx is proportional to this thickness and to the number of γ-quanta incident on the substance. The absorption of electromagnetic radiation is described by the equation

$$\mathfrak{I} = \mathfrak{I}_0 e^{-\mu x}, \tag{5}$$

where $\mathfrak{I}_0$ - the incident radiation intensity; $\mathfrak{I}$ - the intensity of radiation after passage through a layer of substance with thickness x; μ - the linear absorption coefficient in the given absorber.

The interaction of electromagnetic radiation of not very high energies (<10 MeV) with a substance of small atomic number consists almost completely of the interaction with electrons. Three fundamental processes of interactions are distinguished (Fig. 1a, b, c).

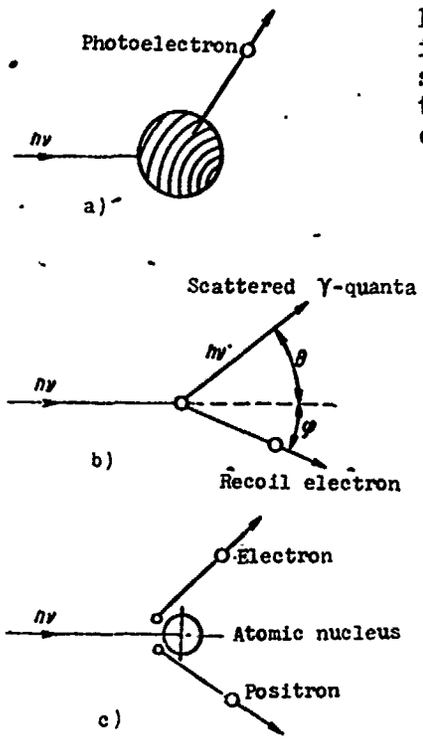


Fig. 1. The processes which flow during interaction of γ-radiation with a substance: a) photoelectric absorption; b) Compton effect; c) formation of electron-positron pair.

Photoelectric absorption. This phenomenon makes the fundamental contribution to the absorption of x-rays and γ-radiation of low energy. During photoelectric absorption the radiation, interacting with a bound electron, dislodges (see Fig. 1a) it from the atom (usually from the K- or L-level). The kinetic energy of the dislodged electron is equal to the difference between the quantum energy of radiation hν and energy E_B of the bond of the electron in the atom

$$E_{e^-} = h\nu - E_B. \tag{6}$$

The vacant place which remained in the electron shell after the emission of the photoelectron is occupied by an electron from an adjacent shell; in this case a new vacant place is formed and the process is repeated many times. Such electron transfers are accompanied by the emission of quanta of characteristic (fluorescent) x-radiation.

The effective cross section of the interaction σ_A of this process can be expressed by the following equation

$$\sigma_A \approx K\frac{Z^4}{(h\nu)^3}, \tag{7}$$

where K - empirical constant; hν - the quantum energy of radiation. From equation (7) it is evident that photoelectric absorption is developed most strongly in heavy elements during irradiation by quanta of low energy.

Compton effect. This phenomenon consists of the interaction of γ-quanta with a free electron.[1] The incident γ-quantum transmits

[1]Usually the energy of the impinging γ-quantum is very great as compared with the ionization energy of the atoms of the scattering substance, therefore scattering can be considered as a process which flows with the participation of free electrons.

part of its energy to the electron which escapes at an angle ϕ in the incident direction of the γ-quantum (see Fig. 1b). The scattered γ-quantum, having lost part of the energy, also changes direction of movement by angle Θ. Energy of the scattered γ-quantum E' is bound with its original energy E_0 and angle Θ by the approximate relationship

$$E' \approx 0{,}51 \frac{E_0}{0{,}51 + E_0(1 - \cos\Theta)}. \quad (8)$$

The γ-quanta scattered as a result of the Compton effect interacting with substance, continue to lose energy further. The final stage of their disappearance is usually photoelectric absorption. The energy of the recoil electron E_e is practically equal to the energy difference of the original and scattered γ-quanta.

It is essential to note that during the Compton effect a γ-quantum with low energy transmits to the recoil electron neglible energy, whereas a γ-quantum of high energy can transmit to the electron almost all its energy.

The formation of an electron - positron pair. If the energy of the γ-quantum exceeds 1.02 MeV ($2m_0c^2$), the process of pair formation is possible (see Fig. 1c). The formation of pairs should occur in the Coulomb field of the nucleus. The energy difference of γ-quantum and the energy which corresponds to the rest mass of the pair of formed particles passes over into the kinetic energy of the pair. The process of pair formation is accompanied by the annihilation[1] of positrons and electrons, during which an energy of $2m_0c^2$ is communicated to two γ-quanta of annihilation radiation (each with an energy of 0.51 MeV).

[1]Annihilation is the interaction of a particle and anti-particle which is accompanied by their transformation into other particles, whereupon the general mass, energy, pulse, and charge of the system are preserved.

The probability of the process of pair creation increases proportionally to the logarithm of the energy of γ-quanta and the square of the atomic number (Z^2) of absorber. Therefore this process acquires the greatest value for materials containing heavy elements.

The process of total absorption of γ-quanta represents the sum of all three effects: photoelectric absorption, dominate for x-rays and γ-radiation of low energy, the Compton effect, which has the greatest value for γ-quanta of intermediate energy, and the process of formation of an electron - positron pair, in which mainly γ-quanta of very high energy participate. The relative contribution of each of these processes for water and carbon is shown in Fig. 2a, b.

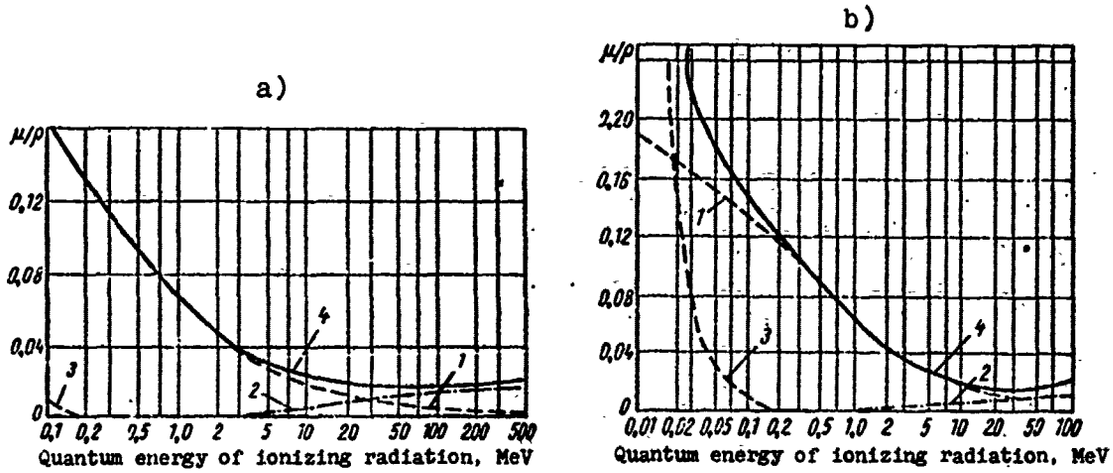


Fig. 2. The contributions of the photoeffect, Compton effect, and pair formation to the mass absorption coefficient μ/ρ during the absorption of electromagnetic radiations of different energy for water a) and for carbon b): 1 - Compton effect; 2 - pair formation; 3 - photoeffect; 4 - total absorption.

BASIC RADIOCHEMICAL PROCESSES TAKING PLACE IN POLYMERS DURING IRRADIATION

The effect of ionizing radiations gives rise to such substantial changes in properties of a substance that these changes acquire noticeable value even in purely technical applications [4-8]. The initial cause of the change in the properties of a substance during interaction with high-energy radiations is the onset of a varying kind of disarrangement of structure (defects in the crystal lattice and processes induced by radiation). Today the following conditional classification of such disarrangements has been accepted in the general sense of the word: a) vacant sites (vacancies); b) atoms incorporated in interstices (intrusion); c) thermal peaks; d) impurity atoms; e) the effects of ionization and excitation; f) peaks of displacement; g) disarrangement induced by collisions during replacements. Let us examine briefly the fundamental features of the disarrangement of the indicated types.

Vacant sites (vacancies) can be formed during the collision of fast neutrons, fission fragments of nuclei and other fast particles with atoms in the crystal lattice of the substance. Usually the energy of the recoil atom proves to be sufficient so that during subsequent collisions it could create additional vacant sites.

Atoms incorporated in interstices (incorporation) are the atoms which were displaced from equilibrium, stable positions in the lattice; if they do not recombine instantly with adjacent vacant site, then they can remain for a sufficiently long time in an intermediate, unstable position.

Thermal peaks. The disarrangement of a structure of this type is conditioned by the vibrations of lattice points. Vibrations appear along the track of the fragment of the nucleus which emerged during division, or of a charged atom (ion) which has

been dislodged from its place in the lattice. The lifetime of such a high-temperature area (with a temperature of about 1000°C) which encompasses several thousands of atoms can comprise 10^{-11}–10^{-10} s.

Impurity atoms are formed as a result of the neutron capture by the atomic nuclei of the initial substance or as a result of the nuclear fission of atoms of heavy elements.

The effects of ionization and excitation are conditioned by the interaction of charged particles passing through the substance with the atomic electrons. In many solids ionization and excitation are accompanied by the breaking of chemical bonds, by the formation of free radicals, atomic and molecular ions, by the appearance of color, by the onset of nonsaturation, etc. These effects are most characteristic for dielectrics, ionic crystals, glasses, and polymers.

The peaks of displacement are formed in the final section of the path track of a fast moving atom. Calculations show the following [9-10]: when the energy of a fast moving atom becomes lower than a specific threshold the mean length of the mean free path between the successive collisions which cause displacements approaches in order of magnitude to the distance between atoms. As a result every collision gives rise to the formation of a displaced atom, and the final section of track represents an area which encompasses several thousands of atoms, in which during a very short time the local melting of the lattice and the intensive movement of the atoms of the lattice points occur. This form of disarrangement is apparently important only for heavy metals.

Collision during replacements. If a collision between moving incorporated atoms and the atoms of the lattice point leads to the knocking out of the latter from their places and if the kinetic energy of the ejected atoms is insufficient to move them rapidly from the vacant sites formed by them then they recombine with these vacant sites, scattering their kinetic energy in the form of the temperature vibrations of lattice [11].

The contribution of the indicated forms of disarrangements of structure to the final change in the properties of a substance during irradiation is not identical and it depends strongly both on the features of the substance itself and on the conditions of irradiation, especially on temperature. The latter fact is connected with the possibility of the "annealing" of defects[1] which substantially weakens the effect of irradiation in solids. The fundamental forms of the disarrangement which appear during the effect of radiation of high energy on solids are shown in Fig. 3.

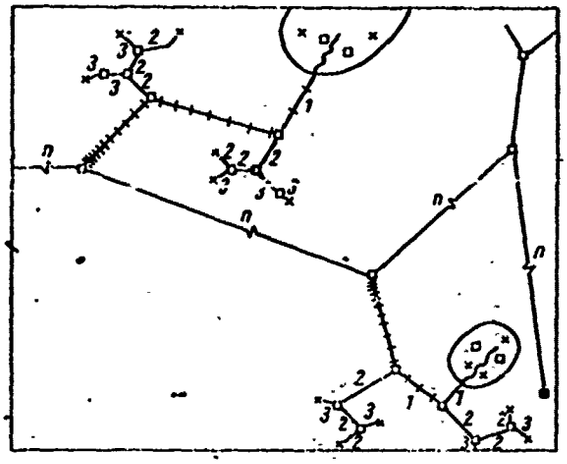


Fig. 3. The fundamental mechanisms for radiation disarrangements: -1-1-1 - ionization; □ - the formation of vacant sites; × - displacement in the interstices; ■ - impurity atom; n - path of neutron; 1 - the path of particle after the first collision; 2 - the same after the secondary collision; 3 - the same after tertiary collision.

Of all the forms of disarrangements of structure indicated above for condensed organic systems the most characteristic are the effects of ionization and excitation, therefore below they will be examined more comprehensively (see also [12-17]).

[1]By annealing is understood the heat treatment of a material in a specific temperature-time regimen.

The Pecularities of Radiochemical Processes

Radiochemical processes are distinguished in principle from photochemical, being also initiated by electromagnetic radiation. This is manifested in a series of specific features caused by substantial differences in energies of light quanta and ionizing radiations.

If the absorption of one light quantum gives rise to the primary excitation of only one-unique molecule of substance, then ionizing radiation (γ-quantum, high-energy electron, and others) spends its energy in the absorber by means of excitation and ionization of a large number of molecules. Under the photochemical effect the excited products are distributed in the bulk of the irradiated substance randomly, whereas under radiochemical they are localized in clots along the track of the ionizing radiation in the substance. Finally the absorption of light quantum converts a molecule only in one-unique of its several possible excited states while the passage of ionizing radiation through the substance can be accompanied by the conversion of many molecules into all the possible excited states permitted for them, and also by the formation of molecular ions. This shows that the initial state of the system after the termination of irradiation is substantially more complex during radiation exposure than during photochemical.

The Distribution of Events of Ionization and Excitation in the Bulk of the Irradiated Substance.

X-radiation or γ-radiation, interacting with the substance by means of creation of an electron - positron pair, by the mechanism of the Compton effect or photoelectric absorption causes the formation of fast electrons in it. The direct irradiation of a substance by accelerated electrons is naturally

reduced simply to their introduction into the irradiated system. Heavy charged particles (protons, α-particles, etc.) lose the greater part of their energy in the irradiated substance, accomplishing ionization and molecular excitation, i.e., transforming it finally into the energy of fast electrons; neutrons spend their energy according to the same mechanism, forming heavy charged particles (recoil atoms, fission products) or generating γ-radiation (radiation capture).

Thus the chemical action of high-energy radiation is almost completely accomplished by rapid electrons independent of the form of primary radiation.

True the nature of the distribution of the initial events of ionization and excitation along the track of the ionizing particle in the irradiated substance to a certain extent depends on its individual peculiarities.

The action of γ-radiation is basically reduced to the formation of Compton electrons, whereupon the points of primary ionization are sufficiently far apart from another. For practical purposes it is possible to consider that Compton electrons are distributed in the absorbing substance according to a random law. As a result of the Compton effect and photoelectric absorption of γ-radiation in light elements fluorescent x-radiation of comparatively low energy is generated. The absorption of this radiation is accompanied by the formation of photoelectrons of low energy near the place of the initial event of interaction. These photoelectrons, as also Compton electrons, generate excited molecules and ions.

The interaction of fast electron with a substance leads to the formation of secondary electrons, which also possess a sufficiently high energy and are capable of interacting with atoms or molecules. With energies below 100 eV, but higher than

the ionization potential of atoms of the absorbing substance (~10 eV) the ionizing and excitation events proceed at a very small distance from primary ions (10 Å in the condensed phase), forming clusters or clots which are usually called spurs. The spurs formed by δ-rays are closely spaced to one another since their energy is less than the energy of primary electrons.

The greatest number of ionizing events in substance are caused by low-voltage electrons; their energy finally falls to a value lower than the ionization potential of the medium and they can now cause only excitation. With the lowering of the energy of the electron to still lower values (lower than the minimum excited level of the absorbing substance) it is able to cause only intraatomic vibrations. When the energy of the electron is lowered to the thermal level (~0.025 eV) it is seized by a positive ion, as a result of which a highly excited molecule is formed.

On the basis of the described process of the loss of energy the track of a fast electron can be presented in the form of a successive series of small randomly arranged spurs divided by intervals. Tracks of δ-particles present an analogous sequence of spurs which are formed according to random law, but arranged closer to each other.

The nature of the tracks of heavy charged particles differs somewhat from that described above, since the events of primary ionization along the path of the particle occur at considerably closer distances to one another. The points of primary interactions are arranged so close that they can be considered as a solid column filled with ionized and excited molecules. Tracks of secondary δ-rays which possess basically low energy are branched from such a column.

During passage through a substance the velocity of ionizing particles is gradually lowered, the density of ionization

created by them increases, and spurs are formed at increasingly closer distances to one another. Close to the end of the tracks the ionization density increases very strongly as a result of the Bragg effect. Slowed-down heavy particles are captured by electrons and are neutralized.

Primary Radiochemical Processes

The fundamental primary result of the effect of radiation of high energy on a substance is ionization and excitation of atoms and molecules, whereupon both the ionized and excited molecules can generate free radicals.[1]

Schematically the processes of ionization and excitations can be presented in the following manner:[2]

$$M \rightsquigarrow M^+ + e^-, \quad (9)$$

$$M \rightsquigarrow M^{2+} + 2e^-, \quad (10)$$

$$M \rightsquigarrow M^*. \quad (11)$$

The positive ions which are formed in the track or spurs should finally be neutralized. The probability of the formation of negative ions in a medium of hydrocarbons as a result of the "adhesion" of an electron to a neutral molecule is sufficiently small and it does not have to be considered.

In general primary ionization leads to the formation of molecular ion either in the normal or excited state. If the ion was formed in the excited state, then it can dissociate up to recombination

$$M^{+*} \rightarrow A^+ + B. \quad (12)$$

[1]Free radicals are molecules or atoms containing an unpaired electron and possessing high reactivity because of this.

[2]In the given reactions the small zigzag arrow designates the interaction of molecule M with the ionizing radiation, and the mark * designates the excited state.

where A+ and B can be the ion-radical and the free radical respectively. Dissociation can also flow according to the mechanism of molecular disproportionation with the formation of a molecular ion and the molecule

$$M^{+\bullet} \rightarrow M_1^+ + M_2. \qquad (13)$$

One of molecules M_1 or M_2 is unsaturated.

In a system containing molecules of two types the molecular ion can be interchanged in charge with a molecule which has a lower ionization potential:

$$M^+ + A \rightarrow A^+ + M. \qquad (14)$$

With the recombination of the ion with an electron a molecule is formed which is found in a highly excited state.

The behavior of doubly charged ions in a condensed system can be developed in one of two directions. The first consists of the splitting of the ion into two fragments, each of which is a positive ion (the realization of this direction facilitates the repulsion of both positive charges)

$$M^{2+} \rightarrow A^+ + B^+. \qquad (15)$$

The second direction is reduced to the exchange reaction of charges which leads to the formation of two singly charged molecular ions

$$M^{2+} + M \rightarrow 2M^+. \qquad (16)$$

This reaction can flow in the case when the ionization potential of formation of M^{2+} more than doubles the ionization potentail of formation of M^+.

The molecular excitation during the action of ionizing high-energy radiation can occur by two paths. The first is the already mentioned process of the neutralization of positive ions by electrons or negative ions with the formation of molecules in

a state of high excitation. The second is the direct molecular excitation during the interaction with high-energy particles. The molecule is excited not in its separate parts, but as a whole, whereupon in large molecules the subsequent reaction of its transformation can flow in a sector which is considerably distant from the place directly affected by the exciting particle.

One ought to keep in mind that the original excitation emerges mainly in electron levels, and the breaking or reconstruction of the bond of the molecule assumes the transmission of this energy to vibration levels. Therefore precisely the probability of the transmitting of electron excitation to vibration levels also determines finally the direction of processes proceeding in the excited molecule.

The excitation energy can also be transmitted from some molecules to others.

The Secondary Radiochemical Processes

The secondary processes follow the events of primary ionization and excitation and condition the final changes in the chemical structure of the irradiated system.

Excited molecule M*, formed as a result of the event of the primary excitation or recombination of an ion, can dissociate into two radicals or into two molecular fragments

$$M^* \rightarrow R\cdot_1 + R\cdot_2, \quad (17)$$
$$M^* \rightarrow M_1 + M_2. \quad (18)$$

Part of the excitation energy can be converted into kinetic energy of the products of dissociation. The radicals which possess high kinetic energy are usually called "hot."

If the excited molecule M* dissociates into molecular fragments, then the final products of the interaction of ionizing

radiation with a substance (radiolysis) are also molecules. If the process of dissociation into radicals occurs then the free radicals formed can enter into reactions of the following fundamental types:

1. **The reactions of recombination.** These reactions flow mainly in spurs where the concentration of free radicals is very high:

$$R\cdot_1 + R\cdot_2 \rightarrow M, \tag{19}$$

$$R\cdot_x + R\cdot_y \rightarrow M_z. \tag{20}$$

The reaction (19), reverse of reaction (17), describes the process of the recombination of free radicals and leads to the formation of the initial molecule M, i.e., it does not cause chemical changes in the system being irradiated. Reaction (20) describes the process of the interaction of two free radicals, as a result of which a new molecule M_2 which is different from the initial is formed. The activation energy of the process of the recombination of radicals is usually very low (and in a number of cases it is equal to zero), but the influence of steric factors can strongly decrease the probability of the course of this process. The concentration of free radicals and their mobility are also important factors.

2. **The reactions of disproportionation.** Reactions of this type usually flow with the transmission of an atom of hydrogen. For instance, two ethyl free radicals, uniting according to reaction (20), can form a molecule of butane

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_4H_{10} \tag{21}$$

or disproportionate with the formation of ethylene and ethane

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_2H_4 + C_2H_6. \tag{22}$$

The activation energy of such reactions is small, whereupon they are strongly exothermic as a result of the liberation of the

extra energy which is freed during the formation of double bond. The reaction of disproportionation can also flow during the interaction of the other various free radicals.

3. **The substitution reaction.** Free radicals can enter into reactions with molecules of unsaturated compounds (both directly in the spur and also beyond its limits) with the transformation of this molecule into the free radical

$$R\cdot + MH \rightarrow M\cdot + RH. \qquad (23)$$

The values of the activation energy of reactions of this type are 5-10 Cal/mole, i.e., the necessary condition for their flow is the exothermicity of the process. The interaction of radical M with the molecules MH in reaction (23) would not bring any changes into the system. Therefore the radicals M·disappear during the recombination of radicals. Specifically, reaction

$$M\cdot + M\cdot \rightarrow MM \qquad (24)$$

lies at the basis of the process of dimerization which is frequently observed during irradiation.

Besides those indicated, several other reactions of free radicals are possible, namely: dissociation, i.e., the decomposition of radicals with the formation of new smaller radicals and molecule, the addition reaction of radicals to the double bond of an unsaturated compound, the reaction of isomerization of a radical, i.e., its intramolecular reorganization with the change of position of free valence, and others.

Ionic-molecular and free-radical reactions will be examined more comprehensively in Chap. II.

THE PECULIARITIES OF ACTION OF IONIZING RADIATIONS ON POLYMERS

The substantial difference in the behavior of low-molecular and high-molecular organic compounds during irradiation amounts to the fact that the physical properties of polymers depend strongly even on small changes in chemical structure. In order to cause the noticeable changes in the hydrocarbon molecule, containing, for example, 20 chemical bonds, it is necessary to change at least one bond, i.e., 5% of their total number. In a long-chain molecule, containing, for example, 10^5 bonds, a change in only one of them can double or cut in half the molecular weight. Chemical changes in this case comprise a total of 0.001%, but sometimes the physical properties change radically for example, viscosity, elasticity, solubility, etc.

During the irradiation in polymers both reversible and irreversible changes of properties can occur.

The primary action of radiation is reduced to ionization and excitation of atoms and molecules which form the given material, whereupon both these processes can lead to dissociation and the breaking of chemical bonds with the formation of ions and free radicals. Further the secondary processes represent the result of the interaction of activated fragments of molecules with each other and with the molecules of the irradiated substance not affected by radiation [18]. Reversible changes in properties are conditioned by the presence in the material, basically, of the initial products of the interaction of radiation with the substance, whereas irreversible changes are the result of those chemical transformations which occurred after the completion of the reactions between the initial products and the surrounding medium.

Reversible processes in the first place are reduced to the appearance of the induced (or radiation) electroconductivity as

well as to the appearance of properties analogous to the properties of semiconductors; these processes gradually disappear after termination of irradiation.

Irreversible processes are connected mainly with the chemical changes in the irradiated system and they are reduced basically to the following effects.

1. Cross-linking - the formation of cross carbon-carbon bonds between the macromolecules of a linear or branched polymer; this process leads to an increase in molecular weight, the formation of a gel fraction (the insoluble part of the polymer) which has a steric structure, and to the corresponding change in the physicomechanical and other properties of the polymer.

2. Degradation - the breaking of the main chain of the polymer molecule; this process leads to a decrease in molecular weight of the polymer and a change in other properties in the direction contradictory to that proceeding during cross-linking.

3. Gas evolution (low-molecular products) - as a result of degradation, dehydrogenation, and the breakaway of side chains of a macromolecule hydrogen and some low-molecular hydrocarbons are liberated.

4. Change in the degree of nonsaturation - the disappearance and formation of different types of double carbon-carbon bonds.

5. The formation of intramolecular bonds (cyclization).

6. Oxidation, leading to the formation of peroxides, hydroperoxides, and other products.

7. Dimerization and polymerization, including graft copolymerization and others.

Along with irreversible chemical changes there are changes in some physical properties for example, the degree of crystallinity, the index of fluidity of a melt, capacity for crystallization from a melt, deformation characteristics, optical and thermophysical properties, etc.

The reversible effects are determined in the first place by the power of the absorbed radiation dose, whereas irreversible - by the absorbed radiation dose.

The changes in the properties of polymers during irradiation are examined in detail in Chap. II.

CHAPTER II

RADIATION CHEMISTRY OF POLYMER SYSTEMS

MECHANISMS OF RADIOCHEMICAL REACTIONS

The absorption of energy of incident radiation in the initial events of ionization and excitation can be considered as a purely physical process. The distribution of the separate portions of the absorbed energy in the thickness of the irradiated substance answers to the law of chance (on the condition that dE/dx is small within the limits of the thicknesses of the substance in question) and does not depend on the chemical structure of the given substance. At the same time the majority of end reactions which are realized during the interaction of the initial products of radiolysis with each other and with molecules of substance not affected by radiation are very specific for the determined chemical groupings.

Therefore along with the examination of the change in the properties of polymers under the influence of radiation there is doubtless interest in a comparison of these changes with the transformation of chemical structure, and also the study of the mechanisms of reactions which lead to such a transformation.

Any chemical reactions in irradiated polymers flow with the participation of the following reaction-capable formations: free radicals, ions, and molecules which are found in the state of electron excitation (excited molecules) [19-24]. Only the free radicals are responsible for the after-effects flowing in irradiated polymers since the lifetime of ions and excited molecules is substantially less.

Reactions Which Flow with the Participation of Ions and Excited Molecules

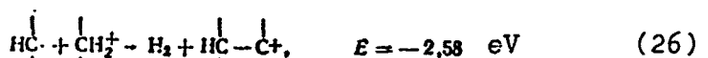
It is very difficult to draw a boundary between the reactions caused by ions (the so-called ionic-molecular reactions) and those initiated by excited molecules.

The distinguishing features of ionic-molecular reactions are: low temperature coefficient; weak influence of phase state; the yield of specific reaction products which are different from the products of free-radical reactions; insignificant influence of the acceptors of free radicals on the yield of reaction products and an increase in yield in the presence of electron traps (for instance, double bonds); correlation with the yields of reactions which flow in the ion chamber of a mass-spectrometer.

In work [25] it has been shown that as a result of ionic-molecular reactions, which can be endo- and exothermic, various products are formed:



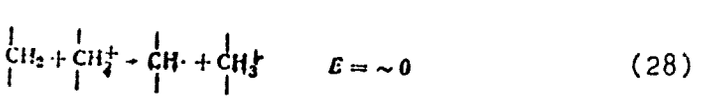
$$E = +0{,}036 \text{ eV} \qquad (25)$$



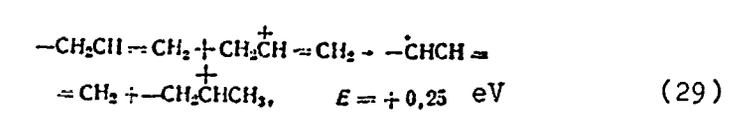
$$E = -2{,}58 \text{ eV} \qquad (26)$$



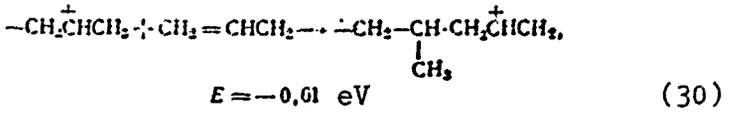
$$E = +0{,}24 \text{ eV} \qquad (27)$$



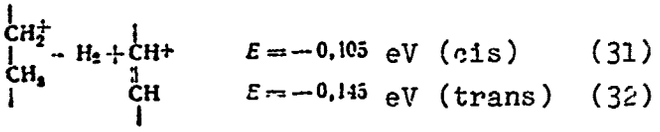
(28)



(29)



(30)



(31)

(32)

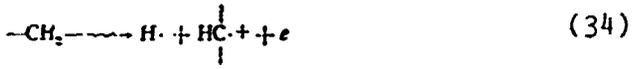
The energy balance of these reactions has been evaluated taking into account the values of ionization potential [26] and the bonding strength [27, 28] in the gaseous phase. Therefore the applicability of the indicated values in the case of a solid or liquid phase is doubtful.

The sequence of ionic-molecular reactions of cross-linking can be presented in the following manner



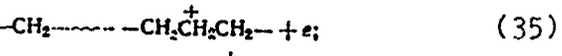
(33)

or

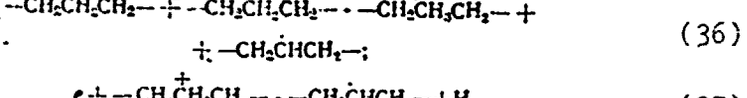


(34)

Then reaction (26) flows when free-radical grouping exists, or reaction (25). Other possible sequences have been proposed in work [29] for pentane and in work [30] for polyethlene



(35)



(36)



(37)

The free radicals which were formed in reactions (36) and (37) then recombine forming a cross bond. Such a sequence of reactions is completely satisfactory because in it mechanisms have been provided by which the molecules scatter the high energy of neutralization up to the level of thermal energy without breaks in the chain, and two free radicals are formed in a convenient position for the flow of reactions of cross-linking. Since the bond length C-C is equal to 1.54 Å and the nearest distance between atoms of carbon which belong to adjacent chains in the crystal of polyethylene is equal to 4.6 Å, the mechanism in which two adjacent atoms of carbon of different chains in a solid polymer can approach sufficiently close and form a covalent bond is quite important. Furthermore the product of any ionic-molecular reaction is an ion, and finally it should be neutralized, and the energy of neutralization - scattered. Although reaction

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + \dot{C}H_3 \qquad (38)$$

and is observed in a mass-spectrometer, it is doubtful that such a reaction with the participation of high-molecular ions, for example

$$C_nH_{2n+2}^+ + C_nH_{2n+2} \rightarrow C_nH_{2n+3}^+ + C_nH_{2n+1}, \qquad (39)$$

can flow in solid polyethylene. If reaction (25) is continued by a chain mechanism, cross-linkages are no longer formed according to random law, and the theories of Flory [31], Stockmayer [32], and Charlesby [33] are inapplicable.

Sufficient proof of the flow of ionic-molecular reactions exists and not only in polymers but also in low-molecular compounds [34-39].

It has been established [40], that during the irradiation of n-1-hexadecene the values of radiochemical yields of hydrogen $G(H_2)$ and trans-vinylene groups G_{TB} are identical and practically do not depend on temperature, phase state, and the presences of acceptors of free radicals. This has also been established for other low-molecular hydrocarbons and polymers [34-39].

In work [40] it has been shown that independent of the site of original ionization in a molecule of n-1-hexadecene the positive charge will probably migrate rapidly along chain to the vinyl double bond, near to which it will be found in a more stable energy state.[1]

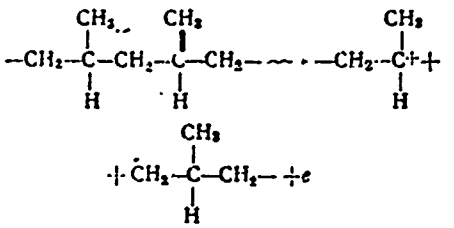
In recent years works have appeared which deal with the study of radiation low-temperature polymerization flowing according to ionic mechanism. It has been established that during the transition from usual temperatures to low the mechanism of radiation polymerization in a liquid usually changes from radical to ionic-cationic or anionic depending on the properties of the monomer and nature of the reaction medium. The carbonium mechanism for radiation low-temperature polymerization has been established for styrene, isobutylene [42, 43], butadiene, and other monomers, and carbanion - for acrylonitrile [44-46]. It has been stated [43] that the initiating particle during radiation polymerization of isobutylene is the positive ion of isobutylene $(CH_3)_3C^+$; in this case a sharp increase in yield is observed in the presence of powder-like inorganic additions.

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[1]Positive ions can migrate to a double bond since the positive charge of a molecular ion in the case of a double bond has an energy state approximately 20 cal/mole lower than in the case of its localization along the main chain; this has been evaluated on the basis of the measurement of the ionization potential of gaseous butane and n-butene [41].

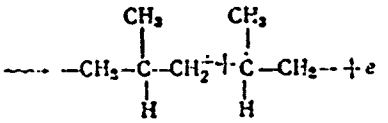
In the studies of Soviet [44-46], and also Japanese scientists [47, 48] the decisive influence of the reaction medium on the mechanism of radiation low-temperature polymerization of acrylonitrile has been shown. The anionic reaction mechanism will be realized only in a medium of substances of a clearly expressed electron-donor nature.

In work [43] it has been shown that in the radiation chemistry of branched hydrocarbons a large role is played by the exothermic processes of the dissociation of ions. For instance, for the radiolytic degradation of the chain of polypropylene there are two possibilities:



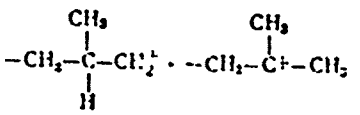
(40)

and



(41)

The ion which is formed in reaction (41) is probably reconstructed into the more stable ion of the *tert*-butyl radical:



(42)

Since reactions (41) and (42) are less endothermic (by 1.2 eV), they should predominate as compared with reaction (40).

In the case of the flow of ionic-molecular reactions the subsequent stages are the stabilization of the products formed and the neutralization of ions. It is assumed that the groups with increased energy level which are formed during neutralization scatter the excess of energy by its transformation into the thermal energy of the surrounding molecules as a result of the Frank-Rabinovich cage effect.[1]

There are data on the transfer of energy from groups which are found in the state of electron excitation to other groups, however, the chemical reactions which flow with the participation of excited molecules have been studied to a lesser degree than ionic-molecular. This is connected with the difficulty of the direct identification of excited products, especially in the condensed phase, and also with the short lifetimes of molecules in excited states.

A reaction which flows with the participation of excited molecules can be examined in the following example.

During the irradiation of the polyethylene Marlex-50 the rapid disappearance of vinyl and also vinylidene unsaturated states is observed. Since the concentration of such groupings in the polymer is substantially less than CH_2 groups, and the absorption of energy of radiation by various groups is equiprobable, it is proposed that this has been conditioned by the transfer of the energy of electron excitation to double bonds [34].

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[1]The essence of this effect lies in the fact that during the irradiation of a substance in liquid and solid states the free radical (or the excited particle formed in the spur) turns out to be as if imprisoned "in a cage" close to the site of formation as a result of collision with the surrounding molecules of liquid (for solids) or as a result of the insufficient mobility of the free radicals and excited particles participating in the reaction.

The mechanism for the disappearance of vinyl groups is the reaction of end cross-linking [35], namely:

$$-CH_2CH=CH_2- \cdots -CH_2\dot{C}H\dot{C}H_2-$$
$$-CH_2\dot{C}H\dot{C}H_2+-CH_2CH_2CH_2- \quad (43)$$

$$-CH_2CHCH_2-$$
$$| \quad (44)$$
$$-CH_2\dot{C}HCH_2$$

or the final product is

$$-CH_2CHCH_2- \quad (45)$$
$$|$$
$$-CH_2CH_2CH_2$$

Furthermore it is supposed that the disappearance of vinylene nonsaturation also occurs with the participation of excited molecules and leads to the reaction of cross-linking

$$-CH_2CH=CHCH_2- \cdots \rightarrow -CH_2\dot{C}H\dot{C}HCH_2- \quad (46)$$

$$-CH_2\dot{C}HCHCH_2-+-CH_2CH_2CH_2- \rightarrow \quad (47)$$

$$\rightarrow -CH_2CHCH_2CH_2-$$
$$| \quad (48)$$
$$-CH_2\dot{C}HCH_2-$$

In reactions (43-48) a biradical (triplet state) participates which is characteristic for any molecule in the state of excitation (electron).

In works [49, 50] it has been shown that the regularities of the accumulation and disappearance of vinyl groups during

the irradiation of polyethylene at low temperatures, the formation of allyl radicals and a system of conjugated double bonds, and also the lowering in their yield by means of the addition of benzene and toluene confirm the substantial role of the migration of the energy or charge during the irradiation of polyethylene.

The lifetime of molecules in the state of electron excitation is very short and electron transitions occur very rapidly; for instance, an electron passes over from a normal state into excited in a time substantially less than one vibration period of a molecule (Franck-Condon principle).[1] With the removal of the atom of hydrogen from the molecule of the polymer it will take away practically all the excess energy in the form of kinetic - it will become a "hot atom." Such atoms can participate in further reactions even at low temperatures. In this case the reactions can be written in the following manner:

$$RH^* \rightarrow R\cdot + H^*, \tag{49}$$

$$H^* + RH \rightarrow H_2 + R\cdot, \tag{50}$$

where the asterisk designates the atoms which possess the excess of energy. The large yield of free radicals during the irradiation of crystalline polyolefins, for example the polyethylene Marlex-50 [23, 51] at a temperature of -196°C, confirms the course of reactions (49) and (50).

---

[1]The Franck-Condon principle consists of the following: the time in which electron transitions are accomplished (as a result of their high speed) proves to be considerably less than the time necessary for any noticeable change in the distance between the nuclei of the vibrating atoms in the molecule.

If the excited state is metastable then the electron converts to the lower excitation level or to the ground level in $\sim 10^{-9}$ s.

Free-Radical Reactions

The presence of free radicals in polymers both during irradiation and after is proved by the results of the study of the superfine structure of the spectra of electron paramagnetic resonance [19-24]. Furthermore after irradiation at low temperatures the free radicals captured in the polymer can be detected chemically by many methods. During or immediately after heating to room temperature it is possible to observe the following reactions: oxidation [52], the initiation of polymerization [53], the isotonic interchange of hydrogen [54, 55], an increase in the yield of cross-linking after the annealing of the irradiated polymer at elevated temperatures [35], liberation of HCl from irradiated polyvinyl chloride at elevated temperatures [56], the acceleration of the disappearance of vinyl nonsaturation [35]. There are proofs [57] that during heating a reaction occurs between molecular hydrogen and polyethylene Marlex-50 irradiated at low temperature. In other words, after irradiation hydrogen is not liberated, but it is absorbed by the polymer, i.e., it is connected to free radicals.

With an increase in the dose of irradiation the concentration of free radicals does not increase linearly but it approaches a certain limiting value. At this stage the rate of disappearance of free radicals not in all cases is equal to the rate of their accumulation, since in the area of very high doses even with the stopping of irradiation the free radicals are not expended for a certain period of time.

In works [19, 23, 58] an investigation is made of the kinetics of disappearance of radicals by the method of electron paramagnetic resonance [EPR] (ЭПР). At small exposure dose two types of radicals were uncovered. One of them, which decayed rapidly, had the structure $\cdot CH_2 \cdot HCH_2$. This was the alkyl radical; it was also uncovered during the investigation of oriented irradiated polyethylene fibers [59]. The nature of the other free radical will be examined below.

Figure 4 shows the rate of disappearance of the alkyl radical in polyethylene Marlex-50 at room temperature in an atmosphere of nitrogen after irradiation up to a dose of 40 Mrad at a temperature of -196°C [60]. It is evident that the kinetic curves can be divided into four linear sections, each of which is subordinated to a law of the first order. The half-lives of the alkyl radicals of these four types comprise 10 s, 25 min, 7.37 h, and 25.2 h respectively. If the reaction mechanism in solid quasi-crystalline polyethylene is subordinated to the same kinetic laws as in homogeneous solutions, then the disappearance of free radicals should occur according to a reaction of the second order. However, as it was shown [34], the kinetics of reactions flowing in solutions hardly can be extended to reactions which flow in solid polymers. It was stated [23] that free radicals are formed by pairs, whereupon the distance between two radicals in every pair is different. If radicals are formed close to one another, they disappear very rapidly, if they were formed at a greater distance from one another they will disappear more slowly. As it will be shown, the process of the disappearance of radicals can flow in a first-order reaction. In work [61] the possibility is examined of the migration of free valence methacrylate; the chain of polyethylene by means of the transmission of an atom of hydrogen from one carbon atom to an adjacent one,

$$-CH_2\dot{C}HCH_2- - -CH_2CH_2\dot{C}H- \qquad (51)$$

This idea has been approved in work [20], and also the proofs of the migration of free valence have been obtained [24, 62]. In the example of 17-pentatriacontane it has been shown that at intermediate temperatures between -196 and 20°C and in the presence of double bonds the alkyl radicals is spontaneously isomerized, probably into an allyl radical.

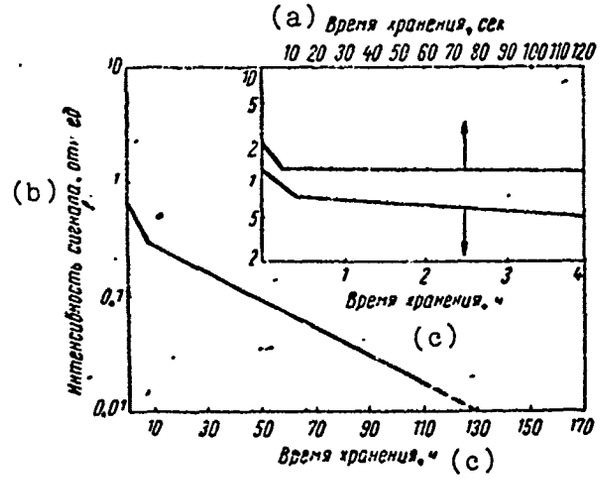


Fig. 4. The dependence of the intensity of the EPR signal for free alkyl radicals in polyethylene Marlex-50 on the time of storage following irradiation.
KEY: (a) Storage time, s; (b) Intensity of signal rel.units; (c) Storage time, h.

It has been established [50] that allyl radicals in irradiated polyethylene correspond to the absorption band in the area of 944 cm^{-1}, observed in the infrared spectrum of absorption only at low temperatures.

Many authors used the EPR method to study the formation and disappearance of free radicals in irradiated polymers: in polyethylene [63-68], nylon [69], polystyrene [66], polymethylmetacrylate [70], polypropylene [62], and in other polymers [71].

In work [72] polyethylene was irradiated in the presence of gaseous deuterium (D_2) at 60°C in a nuclear reactor and it was revealed that after a complement of dose of 400 Mrad the deuterium content in the polymer reached 0.18 mol.%. The authors assumed that isotopic exchange occurred as a result of the following chain reactions:

$$-CH_2\dot{C}HCH_2- + D_2 \rightarrow -CH_2CHDCH_2- + D\cdot; \quad (52)$$

$$D\cdot + -CH_2CH_2CH_2- \rightarrow HD + -CH_2\dot{C}HCH_2- \quad (53)$$

In other works [54, 55] these assumptions were confirmed during the study of the rate of formation of HD in the gaseous phase, when irradiated polyethylene Marlex-50 at -196°C was maintained in gaseous deuterium at room temperature right after irradiation. The analysis of the data obtained during the study of isotope exchange, and also their comparison with the results of works executed by other methods [23, 73, 74], made it possible to show definitely that the second radical which is formed during the irradiation and which plays a significant role in the subsequent reactions, is the allyl type free radical -CHCH = = CH-.

There is important value in the after-effects (i.e., the processes which flow after the termination of irradiation), conditioned mainly by the noticeable lifetimes of the free radicals accumulated in the polymer during irradiation.

Thus in work [52] it is noted that after irradiation in polystyrene and natural rubber considerable oxidation is observed, whereas in polyethylene, polybutadiene, and polyvinyl chloride this effect is substantially less. The comparison of the rate of oxidation of the polyethylene of high and low density showed

that the latter is oxidized very little [75]. On the contrary, linear polyethylene with a high degree of crystallinity absorbs oxygen noticeably at room temperature (Fig. 5). In the figure the concentration of carbonyl groups, calculated by the intensity of the absorption band in the area of 1725 cm^{-1} in the infrared spectrum, is the function of time after irradiation at room temperature. This is conditioned by the fact that free radicals in large quantities and at considerably longer time intervals stick in the polymer matrix of well-ordered linear chains of high-density polyethylene and a high degree of crystallinity.

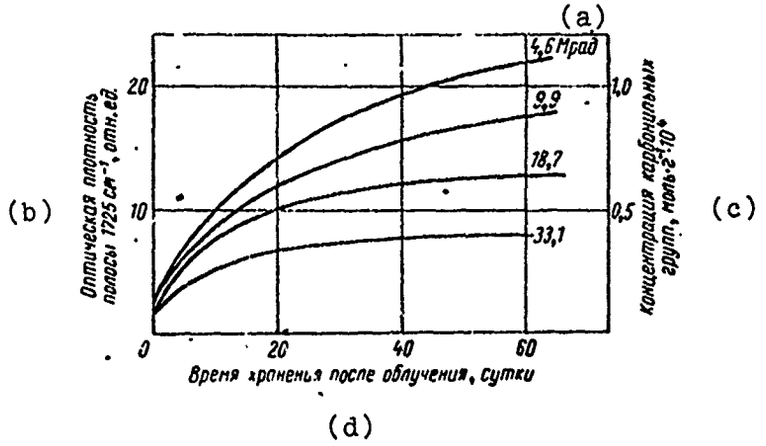


Fig. 5. The change in the concentration of carbonyl groups during the storage of irradiated polyethylene Marlex-50 at room temperature; on the curves the irradiation dose is shown.
KEY: (a) Mrad; (b) Optical density of the band 1725 cm^{-1}, rel.units; (c) Concentration of carbonyl groups, mole $2^{-1} \cdot 10^{4}$; (d) Storage period after irradiation, days.

The after-effect of the oxidation of polyethylene has been quantitatively studied in work [75], and the kinetics of oxidation during irradiation - in work [76].

If the samples of polyethylene are fine films with a thickness of 0.05 mm and less, oxygen can diffuse sufficiently

rapidly into the polymer and react with a greater part of the free radicals in proportion to their formation (which of course also depends on the pressure of oxygen and intensity of irradiation), Under these conditions after-effect of oxidation is neglible even when using polyethylene without an antioxidant [75, 77].

The radiochemical yield of free radicals in the case of the irradiation of highly crystalline polyethylene Marlex-50 at a temperature of -196°C, according to work [23], comprises G = 3.0. This result has been obtained for the irradiation dose of 40 Mrad and it relates to the radicals which do not vanish during irradiation and which enter these or other reactions or recombine. In work [20] for irradiation at a temperature of -80°C the value G = 2.5 ± 0.6 has been obtained.

Free-radical reactions will be examined more comprehensively below in the examples of processes of cross-linking and of the polymer degradation during irradiation.

CHANGE IN THE CHEMICAL STRUCTURE OF POLYMERS DURING IRRADIATION

Cross-Linking and Degradation

Chemical Characteristics

One of the most important characteristics of a polymer is molecular weight. Irradiation can increase or decrease molecular weight depending on which process predominates in the given material - the process of degradation or that of cross-linking. In principle a third process is feasible: in the main chain of the polymer a break occurs and at least one of the fragments

attaches itself to the main chain of an adjacent molecule with the formation of a branched molecule of higher molecular weight. This last process is unimportant, and therefore within the framework of experimental methods the changes in molecular weights can be explained unambiguously with the help of two reactions - cross-linking and degradation [16].

The process of cross-linking represents the formation of the basic chemical bonds between the adjacent macromolecules of a linear (branched) initial polymer and its transformation into a steric polymer. Such a change in structure along with the increase in molecular weight substantially influences all the physicomechanical and physicochemical properties of the material. Thus a polymer which possesses a steric structure does not melt and does not flow at a temperature higher than the melting point of the nonirradiated polymer; it passes over from a thermoplastic into a rubberlike state. The cross-linked polymer loses the capacity to be dissolved in hot organic solvents and will limitedly swell in them. There is a noticeable increase in the stability of the polymer to cracking under stress under the influence of surface-active reagents.

The process of degradation, which is opposite to the process of cross-linking, consists of breaking the primary chemical bonds in the main chain of the polymer molecule. It leads to a decrease in the molecular weight of the initial polymer, the lowering of the melting point, deterioration in physico-mechanical characteristics, and other changes in properties in a direction reverse to the phenomena taking place during cross-linking.

The capacity of polymers for cross-linking or degradation depends on their chemical structure and physical state [18, 78, 79].

Table 2. The influence of radiation on polymers [18, 80, 82-85]

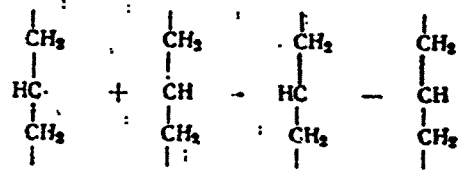
Predominantly cross linking	Predominantly degradation
Polyethylene	Polyisobutylene
Polypropylene	Polyvinylidene chloride
Polyvinyl chloride	Polytrifluorochloroethylene
Chlorinated polyethylene	Polytetrafluoroethylene
Chlorosulphonyl polyethylene	Poly-α-methacrylonitrile
Polyacrylonitrile	Polymethacrylic acid
Polyacrylic acid	Polymethacrylates
Polyacrylates	Polymethacrylamide
Polyacrylamide	Poly-α-methylstyrene
Polyvinylpyrollidone	Polyethylene glycol terephthalate
Polyvinyl alkyl ethers	Cellulose plastomers
Polyvinyl methyl ketone	Casein
Polystyrene	Urea formaldehyde
Sulfonated polystyrene	Melamine formaldehyde
Natural rubber	Polyvinyl formal
Synthetic rubber (besides polyisobutylene)	Phenolic resin without fillers
Polysiloxane	Polyvinyl butyral
Polyamides	
Polyethylene oxide	
Polyethers	
Polyvinyl toluene	
Polyvinyl alcohol	

In Table 2 a classification is given of the most used polymers based on their predominance for processes of cross-linking or degradation.

Attempts to predict sufficiently accurately the behavior of carbon chain polymers of the vinyl series during irradiation led to the following empirical rule [80]: if each atom of carbon of the main chain is connected at least with one atom of hydrogen, i.e., if the polymer has the structure $(CH_2\text{-}CHR)_n$, then in it cross-linking predominates; if the alternating atoms of carbon of the main chain of the polymer are connected with $CH_2\text{-}CRR'$ radicals or by the atoms of other elements, then such polymers predominantly degrade. This rule is only approximate because some polymers, for example polypropylene, have a higher yield of the chain breaks than cross-linking (for isotactic polypropylene $G(s)/G(x) = 1.5$). Furthermore, the relationship of the probabilities of breaks and cross-linking depends on the experimental conditions. For instance, in work [81] it has been established that polyvinyl chloride, irradiated up to a dose of 20 Mrad in a vacuum, remains completely soluble, but if we warm it thoroughly for 10 min at a temperature of 100°C in a vacuum right after irradiation it becomes insoluble. In this case with a dose of 5 Mrad a 65% gel fraction is already formed in polyvinyl chlordie. As a rule the processes of cross-linking and degradation flow simultaneously, but one of them prevails.

The Mechanism of the Cross-Linking Reaction

The most widespread today is the presentation about the process of cross-linking as a result of the recombination of free radicals formed during the irradiation of polymers:



(54)

It has been shown theoretically [86] that radiation creates microzones in the irradiated substance with a considerably higher temperature than the average temperature of the medium. In these microzones favorable conditions appear for a short time for the diffusion of radicals or transmission of valency, as a result of which the free radicals recombine.

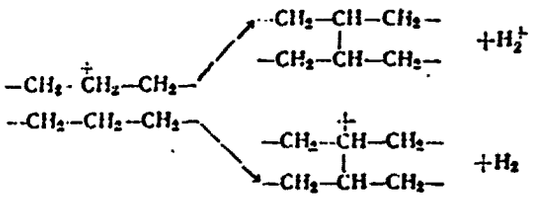
It is known that during the radiolysis of hydrocarbons [see reactions (49), (50)] hot atoms of hydrogen are formed which possess a kinetic energy of 3-5 eV. The atoms of hydrogen with such an energy are able to enter into a reaction with the molecule of hydrocarbon, forming a free radical and a molecule of hydrogen [86-88]. As a result of this process free radicals can be formed in direct proximity to one another and recombine even at relatively low temperatures in the solid phase. Such a mechanism, where during the cross-linking of polyethylene the main role is allocated to the hot atoms of hydrogen, was proposed in works [89, 90].

Those noted above and many other works definitely show that the free-radical reaction mechanism of cross-linking is most probable, this follows at least from that fact that the annealing of a polymer after irradiation noticeably increases the yield of cross-linking. However, it is quite difficult to determine the influence of temperature on the process of cross-linking since there is a lack of reliable and sensitive methods for measuring the degree of cross-linking at room temperature or lower (usually they measure either solubility at elevated temperatures, or swelling or strength characteristics in a rubber-like state). Therefore for the determination of the degree of cross-linking even after irradiation at the temperature of liquid nitrogen the polymer has to be heated to a temperature above room, and this already gives rise to supplementary cross-linking with the participation of the free radicals which are found in the polymer in a frozen state.

These hypotheses, which explain the cross-linking of the molecules of polyethylene by the recombination of the free radicals which are formed in pairs in direct proximity to one another, or by recombination proceeding as a result of the migration of free valence along the chain up to encounter with a free radical, do not agree with some facts, for example, the extremely weak temperature dependence of the yield of cross-linking in interval from -196 to 100°C and the noticeable protective action of a small quantity of additions - the acceptors of free radicals.

These facts have been explained in work [91] by the ionic mechanism of cross-linking because during irradiation induced electroconductivity with a "hole" component appears. Cross-linking, in the opinion of the authors of this work, is the result of the interaction of the mobile hole, which is able to migrate along the polymer chain, with the stabilized free radical of the type $-CH_2-\dot{C}H-CH_2-$, which is accompanied by the splitting of ion H^+. It is possible that here a charged cross-linking is formed which is subsequently neutralized.

In the last work the formation of intermolecular cross-linkings in polyethylene has been examined by the mechanism of ionic-molecular processes

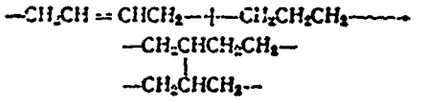


(55)

Such a process in the gaseous phase was observed experimentally [93].

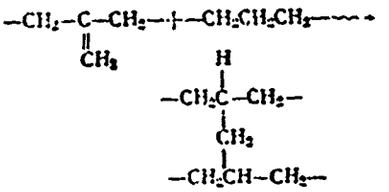
It is possible that the reaction of cross-linking can even flow over the site of a double bond. It was shown [36, 94-96] that the concentration of trans-vinylene double bonds formed (i.e., arranged in the middle of the chain) increases with an increase in the irradiation dose and reaches an equilibrium value. The concentration of double bonds of the vinyl and vinylidene types (in the end and side groups) rapidly diminishes to disappearing small values. In the previous stages of irradiation, when the double bonds of vinyl and vinylidene types disintegrate, the process of cross-linking also flows faster. However, the breaking of double bonds is not connected with the disappearance of radicals. This is shown in the example of the absence of changes in the concentration of vinylene type double bonds, when the free radicals, frozen during irradiation at low temperature, disappear upon heating [95]. Moreover it is proved that nonsaturation does not usually disintegrate as a result of the attachment of molecular hydrogen on the site of the double bonds because the increases in the yield of hydrogen which would correspond to the disappearance of the initial nonsaturation is not observed. It seems that nonsaturation disappears mainly as a result of intermolecular reaction.

If vinylene groups which are chaotically arranged along the polymer chains disappear with the formation of cross-links



(56)

and the vinylidene groups participate in cross-linking by the mechanism



(57)

then the number of cross-linkages formed should be at least equal to or even greater than the number of reacted double bonds. However, this is not confirmed during the determination of the yield of cross-linking based on the quantity of gel fraction formed [97]. This divergence is conditioned by the fact that there is the possibility of the formation not only of molecular bonds (cross), but also intramolecular bonds (cyclization), and also by the fact that the double bonds present in the initial polymer are not arranged chaotically, but mainly in end groups or close to them. In the latter case the formation of end bonds is possible, which will facilitate an increase in the molecular weight of the polymer, but will not condition the appearances of a steric lattice (gel fraction).

Very contradictory data on the mechanism for the cross-linking of polypropylene have been published, for example, in works [98, 99], where values of gel fraction are given which differ within the limits of a whole order.

A certain clarity has been introduced into this question in work [100], the authors of which investigated gel formation in nine various brands of polypropylene. The value of the gel point[1] of the various brands fluctuates within the limits of 8.5-100 Mrad. A study of the viscosity of irradiated polypropylene showed that the high dose of gel formation is caused by the preferential destruction of the chains of polymer in the range of small doses. This preferential destruction is apparently condition by two factors. One of them is presence

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[1]The gel point or the point of initial gel formation is that irradiation dose at which in the polymer already an insoluble fraction appears (gel fraction).

in the chains of polypropylene of oxygen-containing groups. The more that bound oxygen is part of polypropylene, the higher the dose of gel formation (the content of bound oxygen according to radioactivation analysis in the investigated samples comprised 0.01-0.4 wt.%). Another factor is the insufficient quantity of double bonds in the polymer in the early stages of irradiation. Since double bonds in polypropylene are formed precisely during irradiation a certain initial irradiation is necessary for the accumulation of the minimum quantity of double bonds whose interaction with the chains of the polymer would lead to the formation of a gel fraction.

The change in the properties of polypropylene in the beginning of irradiation depends on which of these two factors predominates. A polymer which contains much bound oxygen endures degradation during its irradiation up to the dose of gel formation; the magnitude of the dose of gel formation is determined by the consumption of active oxygen-containing groups during irradiation. In the samples of polypropylene containing an insignificant quantity of bound oxygen, the fundamental determining factor for the dose of gel formation is accumulation of double bonds in the polymer. Here the molecular weight of polypropylene has great significance: the less the molecular weight of the polymer the greater the number of molecules which should suffer destruction for the formation of the necessary quantity of double bonds. Active oxygen-containing groups in such samples of polypropylene disappear long before the beginning of gel formation and intermolecular bonds begin to be formed in the early stage of irradiation. Thus the mechanism for the radiolysis of polypropylene depends on the molecular weight of the polymer and the content in it of active oxygen-containing groups. In various samples of polypropylene the relationship of these factors is diverse, which is connected with the large scattering in the values of the doses of gel formation.

Methods of Measurement of the
Yield of Cross-Linking

For the determination of the degree of cross-linking of polymers up to doses below the gel point it is possible to use different methods for the determination of molecular weights. The viscometric method is used most frequently.

At higher i. liation doses for the determination of the yield of cross-linking it is possible to use the measurement of gel point. For this purpose the dependence of the content of gel fraction in the polymer on the irradiation dose is determined and the magnitude of the doses of the initial gel formation (the gel point) is found by means of extrapolating the curve obtained to intersection with the axis of abscissae. From the theory of gel formation in polymers as developed by Flory [31] and Stockmayer [101] it follows that the initial gel formation corresponds to the appearance of one cross-linked monomeric link on each numerical average molecule. Then the radiochemical yield of the reaction of formation of cross-links can be expressed analytically through the dose of gel formation

$$G(x) = \frac{1,9 \cdot 10^5}{r\bar{M}_{w_0}}, \qquad (58)$$

where r - the dose of gel formation, Mrad; $\bar{M}_{w_0}$ - the initial weight-average molecular weight; G(x) - radiochemical reaction yield of cross-linking, equal to the number of cross-linkages which were formed during absorption of 100 eV.

The equation given above can be used when cross-linking proceeds according to random law, the weight-average molecular weight of the initial polymer is known, there are no degradations

or any radiolytic reactions which change the molecular weight distribution, for example "end" cross-linking with the participation of vinyl groups, reactive gases are absent, for example O_2, NO_2 (in the presence of O_2 peroxide bridges are easily formed NO_2 can interact with free radicals, etc.), and finally magnitude G(x) does not depend on the irradiation dose.

The precise determination of magnitude G(x) is impeded still more by the following facts. During irradiation at room temperature a certain quantity of cross-linkages is formed and also free radicals which can "stick" in crystallites of polyethylene or ordered structures of isotactic polypropylene. With subsequent heating these free radicals will enter into the reaction and form additional cross-linkages. To isolate the latter from the number formed directly during irradiation is practically impossible. Since it is impossible to determine the degree of cross-linking at room temperature and any measuring method - be it dissolution, swelling, or stretching - envisages the heating of the polymer, the unreacting free radicals accumulated during irradiation will enter into the reaction and form additional cross-linkages in the very process of measurement; therefore prior to determination it is advantageous to anneal the sample of irradiated polymer and to measure the summary degree of cross-linking taking into account the after-effect.

Along with the measurement of gel point the magnitude of the degree of cross-linking can be determined by equilibrium swelling of the irradiated polymer in a solvent. The theoretical formula which determines the coefficient of swelling V (i.e., relationship of the weight of the polymer which is swollen in the solvent to the weight of the dry polymer[1]) takes the form

[1]In this case it is assumed that the polymer is completely cross-linked, i.e., strictly speaking, this is the coefficient of swelling of the gel fraction.

$$V'/_s = (0{,}5 - \mu)\frac{M_{cp}}{\rho v}, \qquad (59)$$

where M_{cp} - the average molecular weight of a segment of chain between two tandem cross-linkages; μ - the interaction constant between the solvent and polymer; ρ - the density of dry polymer; v - the molar volume of solvent.

This approximate formula is inapplicable for the high densities of cross-linkages when the coefficient of swelling is small, and also for weakly cross-linked networks in which a significant quantity of substance is still not connected into the cross-linked structure.

For the determination of the average molecular weight of the segment of the chain between two tandem cross-linkages M_{cp} in highly elastic networks it is possible to use the results of the measurement of equilibrium stress [93]. The relationship between applied force in a calculation per unit of the initial area of sample f and its equilibrium elongation λ can be expressed by the formula

$$f = \frac{\rho RT}{M_{cp}}\left[\lambda - \frac{1}{\lambda^2}\right]\left[1 - \frac{2M_{cp}}{M_{n_0}}\right]. \qquad (60)$$

where R - universal gas constant; T - absolute temperature; λ - relationship of the length of stretched sample to its initial length; M_{n_0} - the initial number-average molecular weight of polymer. The expression $1 - 2M_{cp}/M_{n_0}$ represents the correction for end effects.

Knowing $\overline{M}_{cp}$, the value of G(x) can be calculated according to the following formula:

$$G(\lambda) = \frac{0.49 \cdot 10^6}{r\bar{M}_{cp}}, \qquad (61)$$

where r - irradiation dose, Mrad.

The Mechanism of Degradation

The process of degradation is reduced to the breaking of a chemical bond in the main chain of a polymer under the influence of radiation and the formation of molecules of less molecular weight than the initial molecule. It is possible that during the absorption of energy of radiation many bonds in the molecule are broken, however, the majority of them are restored so rapidly that they cannot be detected. For instance, in the case of polyethylene the energy of the C-C bond is substantially less than the energy of the C-H bond, however, mainly the bond of the last type is broken. Apparently two quite long fragments of the molecule which are formed during the breaking of the C-C bond possess insufficient mobility in solid polymeric matrix and manage to recombine with each other before being removed a significant distance. That fact that during the irradiation of polyethylene of low density, polypropylene, and other polymers including the gaseous products of radiolysis along with H_2 low-molecular hydrocarbons are detected confirms the presence of the irreversible breaks in the C-C bond. In these cases the fragments formed are sufficiently mobile in order to go beyond the limits of the Frank-Rabinovich cage.

In this connection it is appropriate to note that according to mass-spectrometric and other investigations the activation energy of the break in the C-H bond in molecules of the initial material which are found in the state of ionization or electron excitation proves to be less than the activation energy of the break in the C-C bond.

One ought to emphasize that all the cross-linking polymers contain in the monomeric link an atom of hydrogen in the α-position, whereas the destroying polymers do not contain it. It is true that the rule is quite approximate since in some of the cross-linking polymers the yield of destruction is actually greater than the yield of cross-linking (in isotactic polypropylene $G(s)/G(x) = 1.5$).

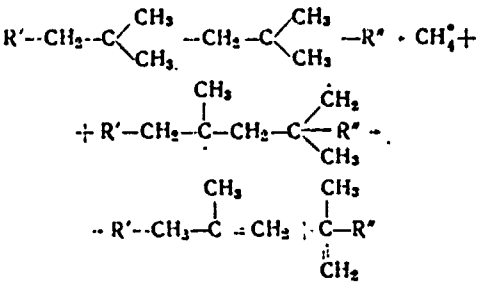
Both processes - degradiation and cross-linking - as a rule flow simultaneously, but one of them prevails over the other.

The mechanism of degradation is determined to a considerable extent by the individual features of the chemical structure of the irradiated polymer and for the majority of substances has not been conclusively established. At the same time the comparison of the results of the analysis of the gaseous products of radiolysis with the data of infra-red and ultraviolet spectrometry along with the assistance of other physicochemical methods of analysis makes it possible to draw certain conclusions.

Thus in work [102] it has been noted that for the polymers which during irradiation undergo predominantly degredation reduced values of the heat of polymerization as a result of steric stresses caused by the presence of substitutes (steric stresses weaken the carbon-carbon bonds in the main chain) are characteristic. These data make it possible to assume that after a quick break of the main chain occurred during irradiation the steric obstacles avert the recombination caused by the effect of the Frank-Ravinovich cage.

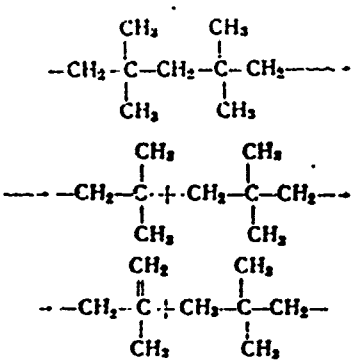
The preferential degradation of polymers is also explained by the possibility of the resonance stabilization of the free

radical which was formed during the breaking of the chain. For polyisobutylene a mechanism has been proposed for the process of degradation which flows with the liberation of one of the substituent groups and the formation of two vinylidene groups for every breaking of the main chain [103]:



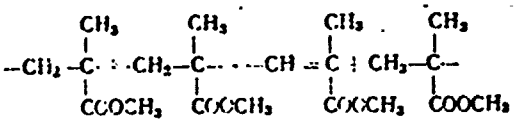
(62)

Also the mechanism for the degradation of this polymer by means of disproportiqnation was examined [104]



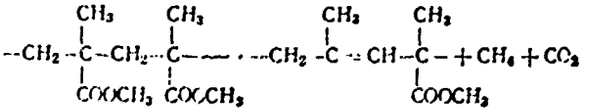
(63)

The degradation of polymethyl methacrylate also can be accomplished with disproportionation [81, 105]



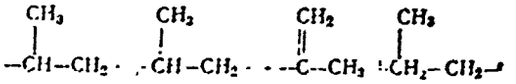
(64)

and also, with equal probability, by another mechanism



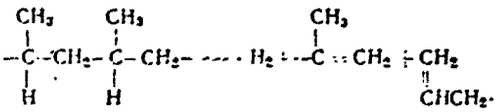
(65)

For polypropylene the following scheme of reaction has been proposed [106], [107]



(66)

However, also feasible is such a path of degradation



(67)

The extensive test data accumulated up to the present time are still the subject of intensified study for the purpose of working out a general approach and establishing distinct regularities.

Methods of Measurement of Yield of Degradation

Degradation in the absence of cross-linking. Let us examine first the determination of the radiochemical yield of degradation G(s) in the case, when the process of cross-linking does not take place. Since the number of molecules in the sample of polymer increases by a unit with every breaking of the chain, the value of G(s) can be calculated easily from the following equality [78]:

$$\frac{1}{\overline{M}_n} = \frac{1}{\overline{M}_{n_0}} + r\frac{G(s)}{100N_A}, \qquad (68)$$

where $\overline{M}_{n_0}$ and $\overline{M}_n$ - number-average molecular weight of polymer before and after irradiation respectively: r - irradiation dose, V/g; N_A - Avogadro number.

The graph of dependence $1/\overline{M}_n = f(r)$ should be straight line with an incline equal to $G(s)/100\ N_A$ and intercept on the axis of ordinates a segment equal to $1/\overline{M}_{n_0}$. For determination of $\overline{M}_n$ it is possible to use any experimental method, whereupon the best is the method of measurement of osmotic pressure. However, the method of measurement of intrinsic viscosity is more accessible.

For the calculation of the value of $\overline{M}_n$ according to the measurements of intrinsic viscosity usually the Mark-Khuvink equation is used:

$$[\eta] = K\overline{M}_n^{\alpha}, \qquad (69)$$

where K and α - empirical constants. The latter can be found by substituting into equation (69) the values of $\overline{M}_n$, determined for the series of samples with various molecular weights by the osmometric method, or by measuring the values of the intrinsic viscosity of the thoroughly fractionated samples of a polymer of known molecular weight. Equation (69) is applicable only when the molecular weight distribution for the given polymer does not change as a result of irradiation and if the form of the molecules remain fixed (branched structures are not formed). If in the initial polymer the molecular weight distribution is most probable and the breaking of chains during irradiation occurs according to random law, distribution by molecular weights for the irradiated polymer remains most probable.

In works [81, 104] the equation (69) was used for the evaluation of value G(s) in the case of the irradiation of

polyisobutylene and polymethyl methacrylate. The results of previous authors have been confirmed in work [108]; there supplmentary data have also been obtained for poly-*tert*-butyl methacrylate. By a combination of methods of light scattering and viscosimetry it has been shown that during radiolysis of the methacrylates cross-linking does not occur.

Degradation simultaneously with cross-linking. In the case of the polymers which undergo cross-linking and degradation simultaneously determination of G(s) presents a serious problem. The measurements of intrinsic viscosity can lead to completely erroneous results for the following reasons: the simultaneous flow of processes of cross-linking and degradation gives rise to a change in the molecular weight distribution, and in this case equation (69) is inapplicable since as a result of cross-linking branched structures are formed, for which constants α and K in equation (69) will change.

Values of G(s) and G(x) can be calculated on the basis of the measurement of the content of gel fraction by using the dependence proposed in work [109]

$$s + \sqrt{s} = \frac{G(s)}{2G(x)} + \frac{50N_A}{rM_{n_0}G(x)} \qquad (70)$$

on the condition that the polymer in the initial state had the most probable distribtuion based on molecular weights, that cross-linking and degradation during irradation occur according to random law, that G(s) and G(x) do not depend on the irradiation dose, and that the initial number-average and weight-average molecular weights are known; in this formula s - the soluble fraction content (sol fraction) in the polymer after irradiation up to a dose of r (Mrad). This dependence is used for many polymers during their irradiation up to doses

higher than the gel point. In work [110] it has been shown that the graph of dependence expressed by equation (70) theoretically has a light curvature with concavity downwards manifested in the area of low values 1/r.

Another independent method of determination of G(s) is based on the measurement of the relaxation of stresses and is used very frequently in the study of rubbers [111]. According to the data of work [112] the number of breaks in chains per gram q is determined by the following equation:

$$q = -1.M_{cp} \lg f/f_0 = -N_0 \lg f/f_0, \tag{71}$$

where f/f_0 - ratio of stresses in the sample before and after irradiation. The value of N_0, reverse of M_{cp}, is determined from the relationship

$$f = N_0 \rho RT (\lambda - \lambda^{-2}), \tag{72}$$

where λ - relative elongation.

Some data on degradation can be obtained from the EPR spectra. Sometimes it is possible to identify the type of free radical and measure its concentration. If free radical has a partial valence on the end of the $RCH_2^{\cdot}$ chain then in the case of linear high-molecular polyethylene this can indicate the flow of the process of degradation. In work [58] they proposed that the stable free radical in polyethylene is the end radical; however, it was shown [20, 71] that the stable free radical in polyethylene is the allyl. During the irradiation of polypropylene quite complex EPR spectra are obtained. This is probably conditioned by the formation of free radicals of various types,

and in this case the presence of end radicals of the type mentioned above does not necessarily attest to the breakings of chains, since such radicals can be formed during the breakaway of hydrogen from the side methyl group.

The Comparison of Values of the Yields of Degradation and Cross-Linking

In Table 3 values of G(s) and G(x) are given which were obtained by various authors with the help of various methods.

Table 3. Some values of the yields of cross-linking G(x) and degradation G(s) (irradiation at room temperature in a vacuum).

Polymer	Method of determination			
	Solubility or swelling	Modulus of elasticity	Solubility or viscosity	Relaxation of stress
	G(x)	G(x)	G(s)	G(s)
Polyethylene				
branched	0.5	1.61		
	1.4	2.4	0.8	
	2.7	3.4-4.6		
	6.8		3.0	
linear	1.02	1.63	1.3	
	2.1	2.4		
Polypropylene				
atactic				
isotactic	0.12-0.27	0.6-1.3	0.1-0.24	
	0.8			
	0.07-0.25		0.1-0.24	
	0.3		0.9	
	0.6		5.0	
Rubber	0.83	1.3	0.8	0.14
Polyiso-butylene	9.3		5.0	
Polymethyl-metacrylate			1.64	
Poly-*tert*-butyl methacrylate			1.67	
			2.33	

The explanation of the quite wide scattering of the values of radiochemical yield of the process of cross-linking obtained by the different authors lies in the fac. that each of them used a different measurement procedure. The accuracy of the absolute values of radiochemical yields of the process of cross-linking is limited by the error of the determination of the average molecular weights of the polymers. The method of the evaluation of radiochemical yield of cross-linking based on content of the gel fraction, which takes into account number-average molecular weight, gives rise to lower values than the method of determination of gel point, which takes into account the weight average molecular weight. The divergence of results can be connected at least partially with differences in doses of irradiation.

The disappearance of double bonds of the vinylidene type which are contained in the initial polymer makes a significant contribution to the process of cross-linking only in low irradiation doses. It is characteristic that the methods of the determination of the yields of cross-linking by measurement of the gel point and the content of gel fraction give rise to satisfactory results during the study of polyethylene of linear structure in which the content of double bonds of the vinylidene type in the initial state is very small.

If hydrogen is liberated from irradiated polyethylene only as a result of cross-linking and *trans*-vinylene nonsaturation,[1] then in the area of very small doses this equation should be correct:

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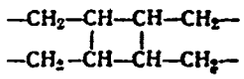
[1]The radiochemical yield of *trans*-vinylene bonds is designated $G_{тв}$, vinyl - $G_{в}$, and vinylidene - $G_{вд}$.

$$G(\text{II}_2) = G(x) + G_{\text{TB}}. \qquad (73)$$

With higher doses the value of G_{TB} diminishes as a result of the disappearance of vinylene groups. If along with direct cross-linking cross-linkages are also formed as a result of this reaction, the dependence given above will no longer be valid.

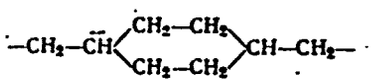
Such a balance is observed far from always and this can be explained by the diversity of flowing processes. Among their number let us point out the following fundamental paths for the realization of competing reactions.

1. The formation of a quadratic bond (the cross-linkages of two contiguous atoms of carbon)



- such a bond will be developed as one cross-linkage.

2. The formation of cycles as a result of intramolecular cross-linking, for example



3. The formation of the system of the conjugated double bonds, for example dienes, trienes, and also cis-vinylene bonds.

4. The flow of degradation, as a result of which the dose of gel formation increases and the value of G(x) calculated by this method turns out to be lowered.

The Change in Nonsaturation During Irradiation

One of the very important changes which takes place in the chemical structure of polyolefins and other polymers during the action of ionizing radiations is the change in the concentration and nature of nonsaturation. In many polyolefins, including in polyethylene, already as a result of synthesis as a rule double bonds are contained, whereupon their type and concentration depend on the method of obtaining the polymer.

In Table 4 data are given on the nature of nonsaturation in samples of polyethylene synthesized by various methods [49].

Table 4. The nature of nonsaturation in samples of polyethylene.

Polyethylene	Quantity of double bonds per 1000 atoms of C	Distribution of nonsaturation by types, % total amount		
		vinyl $RCH = CH_2$	vinylidene $R\diagdown\ \diagup R'C = CH_2$	*trans*-vinylene $RCH = CHR$
High density	0 57	54	31	15
Low density	0.36	13	65	22
Obtained by the method of radiation polymerization	0.05	-	100	-

During irradiation on polyethylene double bonds of the *trans*-vinylene type are accumulated, whereupon their content in porportion to the increase in the irradiation dose reaches a certain limiting value; simultaneously the concentration of the double bonds of the vinylidene and vinyl types which are contained in the initial polyethylene diminishes. In polypropylene during irradiation the double bonds of the vinylidene and vinyl types

appear, and also internal double bonds $\begin{matrix} R \\ R \end{matrix}\!\!>\!C = CHR$ [113]. There is an assumption [107] that as a result of the breakaway of the side methyl groups from the chain of the polymer *trans*-vinylene double bonds can also be formed.

The presence of nonsaturation in a macromolecular chain has a strong influence on the properties of polyolefins. The formation of nonsaturation has important value when using a polymer as an electrical insulating material. This process is accompanied by an increase in the tangent of the angle of dielectric losses in the case of very high frequencies, and it also facilitates the course of oxidizing destruction, if exploitation is conducted in the presence of air at increased temperatures [61, 104, 114].

Many authors [34, 35, 49, 76, 115-121] studied the kinetics and the mechanism of formation and consumption of double bonds in polyethylene. Typical curves of the accumulation and disappearance of nonsaturation in polyethylene Marlex-50 are shown in Fig. 6. In work [34] in an example of three various types of polyethylene it is shown that the formation of *trans*-vinylene groups follows the law of zero order, and consumption - a law of the first order; a stationary concentration is reached when the rates of formation and disappearance are equal to one another.

The concentration of *trans*-vinylene groups in polyethylene Marlex-50 increases somewhat, if after irradiation at room temperature they are annealed in a vacuum [77, 122].

The initial value of radiochemical yield of vinylene groups G_{TB} for linear polyethylene Marlex-50 at room temperature is equal to 2.4, and at a temperature of 142°C it is equal to

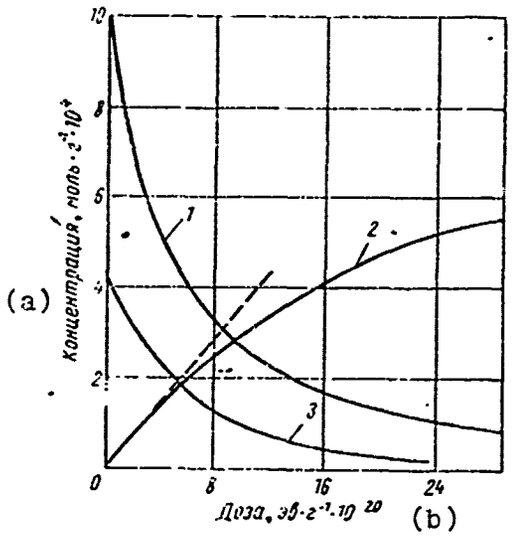


Fig. 6. The dependence of the concentration of double bonds of various types in polyethylene Marlex-50 on the irradiation dose: 1 - vinyl; 2 - trans-vinyl [sic]; 3 - vinylidene.
KEY: (a) Concentration, mole·g^{-1}·10^4; (b) Dose, eV·g^{-1}·10^{20}.

3.1 [35]. At the same time it has been established [49, 123] that the value of G_{TB} increases very weakly with a temperature increase during irradiation from -196 to 20°C. It is difficult to divide the summary yield of vinylene groups into components, conditioned by the splitting of molecular hydrogen from polymeric macromolecules in the state of ionization or electron excitation, on the one hand, and by free-radical reactions on the other. Probably the component which does not depend on temperature is conditioned by the molecular splitting of hydrogen.

As shown in work [34], the concentration of *trans*-vinylene groups in polyethylene Marlex-50 during irradiation up to a dose of 50 Mrad at a temperature of -196°C comprises 0.79×10^{-4} mole/g, and saturation concentration in the case of irradiation at room temperature up to very large doses - 0.71×10^{-4} mole/g. The greater yield of *trans*-vinylene groups at low temperatures

is probably conditioned by the fact that the process of their disappearance depends more strongly on temperature than the process of formation.

The investigation of changes in the chemical structure of polyethylene [124] of low and high density (Marlex-50 and DYNH) showed that for obtaining the same degree of unsaturation of the *trans*-vinylene type a polyethylene of low density (branched, containing vinylidene, *trans*-vinylene, and in an insignificant quantity vinyl groups) has to be irradiated up to a greater dose than linear (with a small content of *trans*-vinylene groups and high concentration of vinyl groups).

In the works [34, 115] it was shown that the vinyl groups which are present in the initial polyethylene Marlex-50 in a concentration of 0.9×10^{-4} mole/g disappear rapidly during irradiation at room temperature, whereupon the yield of this process is $G_B = 9.6$.

As it was established by investigations over a wide range of temperatures [49], during the irradiation of polyethylene the vinyl double bonds not only disappear, but also are formed, whereupon a temperature increase in the polymer during irradiation favors the flow of the process of destruction of this type of nonsaturation.

The increase in vinyl nonsaturation during irradiation was also revealed in work [124], whereupon the rate of formation of vinyl groups was identical in polyethylene of high and low density.

In amorphous polypropylene, irradiated at -196°C up to very high doses (4000 Mrad), they detected [113] the formation of internal double bonds of the type RRC = CHR. Their appearance

was explained by the breakaway of two atoms of hydrogen from adjacent atoms of carbon. Such a type of bond is formed 3.5 times more than end double bonds. In the area of not very high doses, when the regularity of chains is preserved, internal double bonds are formed basically in the *trans*-configuration. With an increase in the irradiation dose, when the regularity of chains diminishes, the formation of internal double bonds occurs basically in the *cis*-configuration. During irradiation the concentration of vinylidene groups diminishes.

The study of the kinetics of accumulation of double bonds during the irradiation of polypropylene showed that after the onset of gel formation the rate of accumulation of double bonds (mainly vinylidene) is less than in the range of small doses [100]. Apparently this is connected with the greater rate of consumption of double bonds after the onset of gel formation. For the clarification of the mechanism of formation of molecular bonds in polypropylene an investigation was made of the influence of various unsaturated additives containing double bonds of specific types on the cross-linking of polypropylene. Since the concentration of double bonds in the additive will react mainly, which will hinder the formation of intermolecular cross-links in the polymer. In this case it was established that the gel point is shifted most strongly to the side of large doses by the additive 2-methyl-butene-1, in the presence of which gel formation is begun only after irradiation up to 150 Mrad. Gel formation is also delayed in the case when in any manner the double bonds formed in the polymer are destroyed. Thus vinylidene double bonds in polypropylene are expended in the reactions of formation of molecular bonds. This is probably conditioned by their higher mobility, and also by presence in the structure of such a grouping of the quaternary atom of carbon, which facilitates the localization of the excitation energy on the double bond.

It is known that during the irradiation of rubbers conjugated bonds are formed in the polymer chain: diene and triene systems [36]. In work [58] they established that polyethylene Marlex-50 after irradiation up to a dose of 2000 Mrad at room temperature acquired a yellow shade and had weak absorption bands in the ultraviolet spectrum at 275, 285, 307, and 322 to 356 mμ. These absorption bands can be conditioned by trienes and higher polyenes. In the infrared spectrum of irradiated polyethylene an absorption band is observed [125] in the area of 985 cm^{-1} which appears during the irradiation of polyethylene up to a dose greater than 50 Mrad and *trans*-conjugated dienes -CH = CH-CH = CH- were assigned to it.

With the help of ultraviolet spectrometry the formation of polyenes $CH_3(CH = CH)_nCH_3$ has been shown with n from 2 to 5 in linear polyethylene [116]. The formation of dienes occurs at a much greater rate than it is possible to expect on the strength of the law of chance and is disproportional to the concentration of vinylene groups. Several mechanisms have been proposed for the formation of polyenes.

The mechanism of formation of *trans*-vinylene groups is represented differently by various authors [117]. One of the proposed mechanisms is reduced to the interaction of two alkyl radicals

$$2\,(-CH_2-\dot{C}H-CH_2-CH_2-) \rightarrow -CH_2-CH_2-CH_2-CH_2- + -CH_2-CH=CH-CH_2- \qquad (74)$$

It is assumed that *trans*-vinylene groups can also participate in cross-linking [117].

On the basis of the study of radiolysis of solid paraffins in work [118] the conclusion is made that cross-linkages between chains are formed as a result of the recombination of allyl radicals.

The process of formation of *trans*-vinylene groups was considered as a process completely distinct from cross-linking, and it was assumed that double bonds during irradiation are formed by means of the extraction of two adjacent atoms of hydrogen as a result of one primary radiation event [115]. This point of view, extended also to the process of formation of vinyl type double bonds, is presented in work [49]. The regularities of accumulation and disappearance of vinyl groups in the opinion of these authors testify to the substantial role of the migration of energy or charge during the irradiation of polyethylene.

One of the possible mechanisms of the formation of *trans*-vinylene double bonds is the migration of free valence along the chain up to an encounter with another free valence, for example

$$\begin{array}{l}\text{—CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{—CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{—} \rightarrow \\ \rightarrow \text{—CH}_2\text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_2\text{—}\end{array} \qquad (75)$$

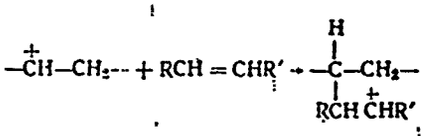
Such a process is exothermic (52 cal/mole) [77, 122]. It is possible that an increase in the concentration of vinylene groups after irradiation is the result of the isomerization of vinyl and vinylidene groups.

The mechanism for the disappearance of *trans*-vinylene groups also is not very clear. They assume [34] that this type of double bond disappears during cross-linking in the reaction

$$\begin{array}{l}\cdot\ \text{RCH} = \text{CHR}' \rightarrow \text{R}\dot{\text{C}}\text{H}\,\dot{\text{C}}\text{HR}' \\ \qquad\qquad\qquad\

This mechanism is reduced to the transfer of energy of electron excitation from the polymethylene chain to the double bond, which is activated and participates in the cross-linking as shown above.

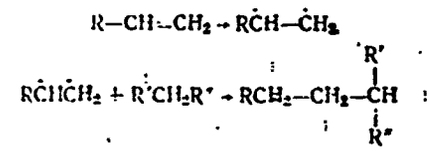
Along with free-radical processes an analysis was made [40] of ionic-molecular reactions of the disappearance of *trans*-vinylene groups



(77)

This reaction can be continued as a chain.

The disappearance of vinyl groups can occur in the processes of free-radical polymerization, isomerization of olefins, or during cyclization [124], and also in the presence of reactions of end cross-linking



(78)

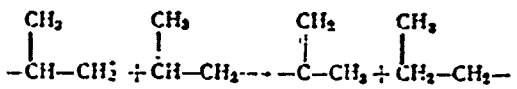
The ionic-molecular mechanism described above [40] is also a variety of the reaction of end cross-linking and can be responsible for the disappearance of vinyl groups.

The thorough experimental investigation [126] of the decrease in the number of vinyl groups in polyethylene Marlex-50 and theoretical calculations showed that the most probable mechanism for the disappearance of vinyl nonsaturation is the reaction of ionic-molecular dimerization.

According to the data of work [35], the disappearance of vinylidene groups takes place according to a law of the first order with the same rate constant of reaction as for vinyl groups. This made it possible to assume that also the mechanism for their disappearance should be similar to the mechanism for the disappearance of vinyl groups, especially it should give rise to cross-linkage.

Apparently not all vinylidene bonds participate in cross-linking [35], since the vinylidene groups are localized near the ends of molecules, and the terminal bonds are formed easier than crossed. Furthermore there is the possibility of the formation of intermolecular cross-links or rings which cannot be detected by measurement of the gel fraction. Finally the isomerization of double bonds can occur [127-120].

The kinetics of the disappearance of vinylidene groups is especially interesting to observe in the example of isotactic polypropylene. During radiolysis of this material one-and-a-half breaks occur for one cross-linking [33]. This led to the assumption about the flow of the following reaction of disproportionation leading to the breakings [107]:



(79)

The actual relationship of the number of breaks to the number of vinylidene groups formed was 1:1, which also follows from expression (79).

The nonsaturation of polymers in radiation chemistry was investigated with the help of the supplementary introduction into polyethylene of compounds containing allyl and vinyl groups

(triallyl cyanurate, 1.19-eicosanediene, and divinylbenzene), and on the basis of the results obtained a conclusion was arrived at concerning the possibility of the transfer of energy on the chain and the localization of it close to unsaturated groups [120]. In the opinion of these authors *trans*-vinylene groups facilitate an increase in the yield of the cross-linking of a polymer during irradiation.

The investigation of the mechanisms for the formation and consumption of the nonsaturation of various types during the irradiation of polymers is treated in a significant number of works [34, 72, 76, 94, 95, 119, 120, 131-135], however, the experimental data obtained at the present time does not permit the sufficiently simple and unambiguous revelation of the nature of these processes.

Gas Evolution During Irradiation

One of the important chemical processes which proceed in polymers during irradiation is the liberation of the gaseous products of radiolysis.

The most studied is the gas evolution of polyethylene and polypropylene [136, 137]. In Table 5 the compositions are given of gases which are liberated during the radiolysis of polyethylene and polypropylene [136].

These compositions of gases relate to equilibrium solubility in the polymer at 25°C following irradiation. The fundamental gaseous irradiation product of polyolefins is hydrogen. If irradiation is conducted at -196°C all the gases in the sample remain frozen up to the moment of heating the polymer to a higher temperature. It has been shown [23] that in polyethylene Marlex-50 diffusion of hydrogen was detected only after heating of the samples from -196 up to -100°C.

Table 5. The gaseous products which are liberated during the radiolysis of polyethylene and polypropylene, vol. %.

Gaseous product	Polyethylene		Polypropylene		
	linear, 20°C	branched, 20°C	isotactic, -196°C	isotactic, 20°C	Atactic 20°C
H_2	99.7	94.3	97.3	97.2	95.7
CH_4	0.1	0.3	2.2	2.5	3.9
C_2H_4	-	0.4	-	-	-
C_2H_6	0.1	0.5	-	0.1	0.1
C_3H_8	-	0.2	0.3	0.1	0.2
$n\text{-}C_4H_{10}$	-	1.3	-	-	0.1
$Iso\text{-}C_4H_{10}$	0.1	-	-	-	0.1
Pentane	-	0.2	-	-	-
Hexane	-	0.3	-	-	-

It is interesting to note that the composition of the liberated gases reflects the chemical structure of side chains. From linear polyethylene Marlex-50 during irradiation almost pure hydrogen is liberated. During the irradiation of isotactic and atactic polypropylene more methane is formed than during the irradiation of polyethylene. In the case of the irradiation of branched polyethylene six times more butane than propane is liberated; the latter is apparently connected with the fact that in the chain of polyethylene there are side branches in the form of chains made from four atoms of carbon. According to the theory of branching of chains [138] this is the most probable length of the side branches in polyethylene. Furthermore it has been experimentally confirmed [139] that the ratio of the content of ethyl and butyl side groups in polyethylene of low density is equal to 2:1.

In work [140] an investigation is made of various irradiated samples of polymethylene with branches of known length synthesized on the basis of mixtures of the appropriate diazoalkanes. An analysis of the gaseous products showed that besides hydrogen the fundamental gaseous products are the products of the breakaway of the side groups from the chain of polymethylene.

During the irradiation of polyolefins in an inert atmosphere the weight of the polymer is reduced. If polyolefins are irradiated in the air or in a medium which is able to interact chemically with the products of the radiolysis of the polymer (for instance, in the medium of a monomer), then an increase in weight is possible as a result of the attachment of oxygen or a monomer to the molecule of polymer.

With the breaking of the C-C bond two free radicals are formed which can recombine as a result of the cage effect, and in this case they cannot be detected. If they diffused from one another prior to recombination, then each of them can subsequently recombine with the other free radicals. To disproportionate or to be inactivated by means of the breakaway of the atom of hydrogen from the nearest molecule of the polymer

$$2C_3H_9\cdot \rightarrow C_3H_8 + C_6H_{10}, \tag{80}$$

$$2C_2H_5\cdot \rightarrow C_2H_4 + C_2H_6, \tag{81}$$

$$2R\cdot \rightarrow R{-}R, \tag{82}$$

$$R\cdot + H_2\overset{|}{\underset{|}{C}} \rightarrow RH + H\overset{|}{\underset{|}{C}}\cdot \tag{83}$$

The low yield of unsaturated compounds (see Table 5) and also ethane during the irradiation of polypropylene testifies to the preponderance of reaction (83). As can be seen from Table 5,

there is no substantial difference between atactic and isotactic polypropylene - in contrast to linear and branched polyethylene. Since the significant yield of gaseous hydrocarbons in the latter case is explained by the large number of short side branches and end groups in polyethylene of low density as compared with polyethylene of high density, it may be concluded that in atactic polypropylene there are no more end groups than in isotactic [141], although in work [142] it is proposed that the difference in the properties of isotactic and atactic polypropylene is conditioned by the difference in the degree of branching, and not in steric regularity. Really in work [100] it has been shown that atactic polypropylene is branched.

In Table 6 the values are given for the radiochemical yields of gases from polyethylene. Yield $G(H_2)$ for liquid polyethylene at 142°C is equal to 6, i.e., is greater than for liquid n-hexane at 25°C, which is equal to 4.95 [143, 144].

In another work [145] liquid cyclohexane was irradiated by γ-radiation of Co^{60} at temperatures from -60 to 25°C and a value of $G(HD_2) = 5.8$ was obtained. This value does not depend on the temperature of irradiation and is practically identical with $G(H_2)$ for liquid polyethylene at 142°C. On this basis it is possible to assume that the mechanism for the liberation of hydrogen in both cases is identical.

The formation of hydrogen during the radiolysis of polyethylene was investigated in detail [146]. Radiochemical yield $G(H_2)$ drops with a temperature decrease in the indicated range from 5.8 to 4.7; this is explained by the more effective protective action of the products of radiolysis being accumulated at low temperature. The radiochemical yield of hydrogen at room temperature depends on the irradiation dose, whereupon in the

range of doses of 0-60 Mrad the minimum value is observed. A delay has been established in the liberation of hydrogen during the low-temperature radiolysis of polyethylene and low-molecular hydrocarbons. Thus, during the irradiation of polyethylene up to a dose of 6250 Mrad at a temperature of -110°C 95% of entire amount of hydrogen formed in it is delayed. The delay of hydrogen in polyethylene bears a predominantly diffusion nature: in this case it is assumed that hydrogen is accumulated in the places of disposition of the double bonds which have less "molecular volume" in comparison with C-C bonds.

Table 6. Radiochemical yield of gases during the irradiation of polyolefins.

Polymer	Characteristics	Gas	Temperature during irradiation, °C	Radiochemical yield
Polyethylene linear	Solid	H_2	-196	3.0
	"	H_2	25	3.8
	Liquid	H_2	142	6.0
branched	Solid	H_2	-196	3.4
	"	H_2	25	4.1
Polypropylene	Atactic	H_2	25	2.3
		CH_4	25	0.09
	Isotactic	H_2	-196	2.5
		CH_4	-196	0.05
		H_2	25	2.7
		CH_4	25	0.07

The values of the integral yield of the gaseous products of radiolysis of various polymers during irradiation up to a dose of 10^8 rad are given in Table 7.

Table 7. The yield of gas during the irradiation of various polymers [18].

Polymer	Number of molecules per 100 eV
Polytetrafluoroethylene	0.051
Polyisobutylene	0.74
Polyvinyl alcohol	0.96
Polystyrene	0.069
Polymethyl methacrylate	1.11
Polybutadiene	0.23
Polyethylene	2.03
Polyacrylonitrile	0.33
Polymethyl acrylate	2.89
Natural rubber	0.44

The results of the analysis of the gaseous products of radiolysis [147] of liquid branched alkanes made it possible to assume that the simple breaking of the C-C bond does not occur, but this bond is broken predominantly close to the branching point. These conclusions are important for the understanding of differences in the behavior of polymers during irradiation.

THE INFLUENCE OF THE CONDITIONS OF IRRADIATION, PHASE STATE, AND THE PECULIARITIES OF POLYMER STRUCTURE

The Influence of the Medium and Dose Rate

It is known that the medium in which irradiation is conducted has a very strong influence on the physical, chemical, and electric properties of polymers. This has been demonstrated many times in the example of the influence of oxygen on polyethylene and other polyolefins [148-155].

The Influence of Oxygen During Irradiation

During the irradiation of polyethylene in an atmosphere of oxygen (air) the free radicals which emerge react with the oxygen, thus forming various oxidation products.

A comparison of the data obtained in samples with a different relationship of areas and volume (for instance, fine films and grains) showed [150, 156, 157], that oxidation during irradiation is mainly a surface effect.

In work [75] a study was made of the kinetics of oxygen absorption during and after the irradiation of a fine film made from polyethylene Marlex-50 which did not contain an antioxidant. The results of the determination of the gaseous products formed and also the measurements of the quantity of oxygen-containing groups by the method of infrared spectrometry are given in Table 8.

The formation of oxygen-containing groups in a polymer has a negative influence on the yield of radiation cross-linking and lowers the resistance of the polymer to heating.

During the initial stages of irradiation in doses less than 1 Mrad all the dissolved oxygen (which in polyethylene, for example, is quite little) reacts with the polymer. The further course of reaction of oxidation is limited by the rate of diffusion

Table 8. Products which are formed during the radiation oxidation of polyethylene

Gaseous products	Partial pressure, mm Hg	Oxygen-containing products	Relative Content, %
H_2	66.7	RC = O	25
CO	5.7	H_2O	14
H_2O	18.1	CO_2	6
CO_2	4.2	CO	5
		Hydroperoxide and alcohols	50

Note. Polyethylene Marlex-50 unstabilized, film thickness 0.0388 cm, integral dose $6.47 \cdot 10^{20}$ eV/g.

of oxygen into the polymer. At the high dose rates this produces little effect because the dissolved oxygen already reacted, the access of oxygen from without (as a result of diffusion) is not great and irradiation flows practically in an inert atmosphere. At low dose rates oxygen noticeably influences the processes which flow during irradiation in polymers.

The value of radiochemical yield of radiolytic bonding of oxygen in a polymer $G(-O_2)$ depends very strongly on many factors and especially on the thickness of the film of polymer, the intensity of irradiation, and the pressure of oxygen [75, 150, 152, 158]. With an increase in the thickness of film the value of $G(-O_2)$ first increases, reaching a maximum, and then it diminishes, when film becomes already so thick that the oxygen cannot diffuse through it sufficiently rapidly and enter into a reaction with all the free radicals being formed. Peak value $G(-O_2) = 9.9$ for a film thickness of 0.021 cm and an initial pressure of oxygen of 5.5 cm Hg. Using the kinetic equations which take into account both the diffusion of oxygen into sample through the surface and the interaction with the free radicals being formed it was calculated that the peak value of $G(-O_2)$ at a high pressure of oxygen would be equal to 15 ± 3 [75].

Many polymers are very sensitive to oxidative degradation during the irradiation, and even traces of oxygen substantially influence the process of radiolysis. Thus in work [100] it was shown that very small quantities of oxygen (0.01-0.4 wt. %), which are present in polypropylene, are the reason for the degradation of polymer chains in the area of the small irradiation dose.

Further it is known that in the case of the irradiation of polyethylene at room temperature in the presence of air or oxygen the quantity of gel fraction formed diminishes. In Table 9 data are given from work [152] on the influence of the dose rate, pressure of oxygen, and thickness of the film of polyethylene on formation of the gel fraction with a dose of 10 Mrad.

Table 9. The decrease in the content of gel fraction in polyethylene irradiated up to a dose of 10 Mrad in the presence of O_2.

Thickness of film, mm	Pressure O_2, atm	Relative dose rate	Gel fraction content, %
0.32	0	1	52.5
0.36	10	1	19
0.36	10	0.2	14
0.33	10	0.1	6.5
0.33	10	0.05	0

From the available literature data it is not possible to make an unequivocal conclusion whether or not the decrease in gel formation in the presence of oxygen is the result of the inhibition of cross-linking or acceleration of degradation or of both factors simultaneously. In work [159] they assume that degradation increases, and cross-linking is not sensitive to the presence of oxygen. These data agree with the theoretical equation of Charlesby for gel formation during the simultaneous flow of cross-linking and degradation. Nevertheless the authors of work

[160] consider that in the presence of oxygen G(x) diminishes. The modulus of elasticity at 150°C, proportional to the number of cross-links, after irradiation in a reactor in air was four times less than during irradiation in a vacuum.

In work [36] it has been shown that oxygen completely inhibits the formation of dimer during the radiolysis of n-hexane. Apparently oxygen can inhibit the reaction of cross-linking. During irradiation of alkanes with branched chains in a vacuum it was established [147] that breaks of simple C—C bond do not occur, but they are observed near the branching points. In work [161] it is noted that oxygen diminishes the yield of cross-linking and facilitates the course of degradation.

The Mechanism of Radiation Oxidation

The investigation of the mechanism of radiation oxidation of hydrocarbons, including polymers, has been treated in many works.

Thus the data obtained by photooxidation[1] of hydrocarbons [162] could be interpreted, assuming the flow of the following chemical reactions between the free radicals formed under the influence of radiation and oxygen:

$$R\cdot + O_2 \rightarrow RO_2\cdot. \qquad (84)$$

The $RO\cdot_2$ radical can further participate in reactions in two various ways

[1]The differences between radiochemical and photochemical processes (see page 22) do not eliminate the possibilities of the initiation of radical reactions, oxidation for example, if the energy of the light quantum is sufficient for breaking the chemical bond and the formation of a free radical.

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \quad (85)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \quad (86)$$

or

$$R'-\underset{\underset{R''}{|}}{\overset{\overset{H}{|}}{C}}-O_2\cdot \rightarrow R'-\underset{\underset{O}{\|}}{C}-R'' + OH\cdot \quad (87)$$

$$R'CH_2R'' + OH\cdot \rightarrow R'-\underset{\underset{H}{|}}{\dot{C}}-R'' + H_2O \quad (88)$$

$$R'-\underset{\underset{H}{|}}{\dot{C}}-R'' + O_2 \rightarrow R-\underset{\underset{O_2}{|}}{\overset{\overset{H}{|}}{C}}-R'' \quad (89)$$

The activation energy of reaction (85) in the gaseous phase comprises more than 17 Cal/mole. Therefore reaction (85) does not flow at a noticeable rate at temperatures below 100°C, if the $RO_2\cdot$ radical after formation does not possess a significant excess energy. Reaction (87) is exothermic, but probably is characterized by a high preexponential factor in the kinetic equation, and chain reactions (87)-(89) can flow slowly. Peroxides and hydroperoxide are formed in reactions of the type

$$RO_2\cdot + HO_2\cdot \rightarrow ROOH + O_2, \quad (90)$$

$$RO_2\cdot + RO_2\cdot \rightarrow ROOR + O_2. \quad (91)$$

The free $HO_2\cdot$ radical can originate in the reaction

$$R'CH_2R'' + O_2 \rightarrow HO_2\cdot + \underset{\underset{O\cdot}{|}}{R'CHR''}. \quad (92)$$

Ionizing radiations easily generate ozone in the air, therefore reaction (92) flows very intensively.

In work [161] in the examination of the influence of oxygen and peroxides on irradiated polymers the conclusion is made that oxygen can attach itself to the double bonds formed under the influence of radiation; the peroxides obtained in this case then decompose and form two carbonyl groups (water in this case is not formed):

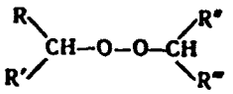
$$RR'CHCHR''R''' \rightsquigarrow RR'C=CR''R''' + H_2 \quad (93)$$

$$RR'C=CR''R''' + O_2 \rightarrow RR'C(-O-O)-CR''R''' \quad (94)$$

$$RR'C(-O-O)-CR''R' \rightarrow RR'C=O + O=CR''R''' \quad (95)$$

Flow and other reactions are possible [75].

The best proof of the formation of peroxides during the irradiation of polyethylene in the presence of air is the following: the polymer which was formed during the action of γ-radiation on vinyl monomers by itself can initiate polymerization after the termination of irradiation, after the loss of its polimerization activity it is possible to again make it an active initiator of polymerization with the help of heating [161, 163-166]. Analogous results were obtained in work [149] by another method. Their explanation is reduced to the fact that during the irradiation of polyethylene in air peroxide bridges were formed in it - unique cross-linkages



Upon heating to 150°C the peroxide bond O—O is broken and at the site of the break free RO• radicals are formed which are able to initiate polymerization.

If hydroperoxide ROOH are formed, then breakings are possible at lower temperatures; they give rise to formation of RO· and OH·. OH· radicals are able to initiate homogeneous polymerization in a solution of monomers while RO· radicals can initiate mainly heterogeneous or graft polymerization.

The Influence of Oxygen After Irradiation (After-Effects)

It was revealed [152] that polystyrene, irradiated in a vacuum up to very high doses (~10^5 Mrad), interacts with oxygen

over a period of several days after direct contact with air. In its infrared spectra an increase is observed in the intensity of the absorption bands which correspond to groups of CO (at 1725 cm^{-1}) and OH (at 3400 cm^{-1}).

Still earlier [77] they observed the oxidation of polyethylene irradiated in a vacuum following its transfer into an air medium. Such post-oxidation of polyethylene of low density was insignificant during irradiation up to small doses. However, highly crystalline polyethylene Marlex-50 was noticeably oxidized after irradiation up to significant doses.

The oxidation process in air after irradiation in a vacuum flows for a sufficiently long time [75, 77]; thus the increase in the intensity of the absorption bands which correspond to carbonyl groups is continued even after 40 days of being kept in air at room temperature.

It is significant to note that polyethylene irradiated in a vacuum in molten state and cooled to room temperature is not oxidized upon contact with air. Hence it follows that oxidation after irradiation is conditioned by free radicals captured in the polymeric matrix. The opinion that the influence of oxygen on a polymer after irradiation in a vacuum is conditioned by interaction with captured free radicals is universally recongized [35, 122, 125, 168-170]. In literature there are some contradictions relative to the nature of these captured radicals and to their localization in the polymeric matrix, but it is doubtless that crystalline polymers following irradiation can capture free radicals for a certain period of time. This is mainfoldly confirmed by the [EPR] (ЭПР) method.

During a comparative study of polyethylene of low and high density it was shown [125, 181] that polymers with high degree of crystallinity develop a greater tendency toward the capture of

free radicals on the surfact of crystallites. Captured radicals can exist in polymers with a high degree of crystallinity for quite a prolonged time and finally disappear as a result of some interaction. Precisely the method by which they interact determines the final properties of the irradiated polymer. For instance, highly crystalline polyethylene Marlex-50 possesses a noticeable capacity to capture free radicals during irradiation. If such an irradiated polymer is then stored in air, oxygen will slowly diffuse into the sample and interact with the free radicals. This gives rise to the incorporation of oxygen in the molecule of polymer as well as subsequently to the reactions of breaking of the polymer chain.

In work [172] they have shown the influence of holding in air of polyethylene Marlex-50, irradiated in a vacuum up to a dose of $1.5 \cdot 10^7$ rad, on physical properties. Tensile and rupture strength during breaking were measured after various periods of holding the samples in air. It was revealed that relative elongation is strongly lowered with an increase in the period of holding in air.

Annealing in inert atmosphere directly after irradiation at a temperature higher than the melting point of crystallites prevents a change in the properties of a polymer during prolonged storage in air [35, 125]. In this case captured radicals manage to react and no longer can participate in reactions with oxygen of the air.

The Influence of Various Gaseous Media

In work [151] they studied the influence during the irradiation of a number of gaseous media (O_2, N_2O, CO, H_2, Cl_2, SO_2, NH_3, NO_2) on the yield of gel fraction and the coefficient of swelling of polymers. The gas pressure during irradiation comprised 600 mm Hg.

It has been established that N_2O somewhat increases gel formation, CO, H_2, SO_2, and Cl_2 practically do not influence this process, O_2 reduces the content of gel fraction from 85-90% at a dose of 50 Mrad (irradiation in a vacuum) to approximately 25% at 20 Mrad, and NO_2 completely depresses the process of cross-linking (the content of gel fraction is practically equal to zero). According to the degree of influence on the decrease in the coefficient of swelling after irradiation under identical conditions these gases can be arranged in the following order: $O_2 > Cl_2 > NH_3 > CO > SO_2$; H_2, N_2O. The results in the decrease in the coefficient of swelling in the presence of NO_2 are not given. These quantitative results probably depend on the solubility of gases in the polymeric film, the rate of their diffusion into the polymer, and the intensity of irradiation.

The noticeable influence of NO_2, which is expressed in the complete suppression of the process of formation of gel fraction in doses up to 50 Mrad [151], is probably conditioned by that fact that $NO_2\cdot$ is a free radical and, as is known, can influence the breaking of chain free-radical reactions. The reaction of the type

$$-\dot{C}H- + NO_2\cdot \rightarrow -\overset{NO_2}{\underset{H}{C}}- \qquad (96)$$

undoubtedly flows at a high rate.

Irradiation in an atmosphere of N_2O is of significant interest. The nitrous oxide exerts a sensitizing action [i.e., increases the yield of the radiation cross-linking G(x)] on the process of radiation cross-linking of polyethylene [173-176], polyisobutylene [177], polypropylene [178-179], the copolymer of ethylene with propylene [179], and polystyrene and polyamide [180]. In works [173-176, 180] it has been shown that during the irradiation of polyethylene in an atmosphere of N_2O an increase

is observed in the yield of cross-linking by 44%, and of *trans*-vinylene bond - by 87% (at a pressure N_2O ~ 600 mm Ht). The gaseous nitrous oxide during the irradiation is expended with a very large yield G = 10^3 with the formation of N_2 and H_2O, the quantity of which stoichiometrically corresponds to the reaction

$$N_2O \xrightarrow{H_2} N_2 + H_2O \qquad (97)$$

The formation of cross and *trans*-vinylene double bonds increases monotonically with an increase in concentration of N_2O in the polymer. Since in polyethylene only 0.1 wt. % N_2O is dissolved, the energy absorption of radiation with molecules N_2O is very low as compared with the energy absorbed by the polymer. The high yield of decomposition of N_2O made it possible to assume that part of the energy absorbed by the polymer is transferred to N_2O molecules and the excited N_2O molecules break away H atoms from polymer segments located in the vicinity:

$$-CH_2-CH_2-CH_2- + N_2O \rightarrow -CH_2-\dot{C}H_2-CH_2- + N_2O^{\bullet} \qquad (98)$$

$$N_2O^{\bullet} + \begin{matrix} CH_2 \\ \diagup \quad \diagdown \\ CH_2 \quad CH \end{matrix} \rightarrow \begin{matrix} CH_2 \\ \diagup \quad \diagdown \\ CH \quad CH \end{matrix} + N_2 + H_2O \qquad (99)$$

or

$$-CH_2-CH_2- \xrightarrow{N_2O^{\bullet}} -CH=CH- + N_2 + H_2O \qquad (100)$$

By the transmission of part of radiant energy absorbed by polymer to the nitrous oxide dissolved in it it is possible to explain the decrease observed in the yield of degradation of polyisobutylene in the presence of N_2O [177].

In the works [167, 178] the sensitizing action of nitrous oxides is connected with the property of N_2O molecules to fulfill the role of electron acceptor.

The Influence of Dose Rate

It was predicted from general considerations that the process of cross-linking of polymers should not depend on the intensity of irradiation [181]. This was shown experimentally [182] on samples of polyethylene of low density during irradiation in a vacuum (residual pressure not higher than ~10^{-3} mm Hg) by fast electrons (dose rate 6, 12, 24, 338, and 2070 Mrad/min). The results obtained clearly show that the quantity of cross-linkages is proportional to the integral dose and does not depend either on the dose rate or the energy of the electrons.

It is necessary to note that only during irradiation in a vacuum was no influence of dose rate observed. During irradiation in air a noticeable dependence on dose rate is observed but in this case the determining role is played by the diffusion rate of oxygen into the polymeric matrix [183]. It must also be noted that at very high dose rates part of radiant energy is scattered in polymer in the form of heat; as a result the temperature of the polymer during irradiation is raised, which can also noticeably influence the reaction yield of radiation cross-linking.

The Influence of Temperature, Degree of Crystallinity, Supramolecular Structure, and Molecular Weight Distribution

The majority of polymers, including polyolefins, represent compound formations with a various degree of order of segments of macromolecular chains. It is considered that ordering at the molecular levels corresponds to a determined degree of crystallinity; the totality of the erratic sections of macromolecules forms the amorphous phase [184]. However, this concept is very conditional and in the last decade underwent a basic review [185-187]. The development of the experimental technique for studying the structure of polymers, especially methods of

electron microscopy, made it possible to reveal large aggregates in them - areas including many molecules - the so-called "supramolecular structures."

It is natural that the degree of order of structure and the level on which this ordering is developed substantially influence the various properties of the polymer and, in turn, depend strongly both on the structure of the polymer chain and on the mobility of the marcomolecular chains and their individual sections or segments, which is determined by temperature.

The molecular weight of a polymer, its polydispersion (distribution by molecular weights), and the conformation of molecules also to a greater or lesser degree determine the relative packing of chains.

In this connection the interest is understandable which is systematically displayed by many investigators in the study of the influence of all the factors noted above on radiochemical processes which proceed in polymers during irradiation.

The Influence of Temperature and Degree of Crystallinity

It has been established that the degree of cross-linking of polyolefins depends on the temperature at which irradiation of the polymer is conducted [34, 73, 89, 123, 125, 163]. Many authors studied this phenomenon on samples of polyethylene with a various degree of crystallinity and observed that the yield of cross-linking in the range from -253 to -40°C does not depend on temperature; in proportion to the further temperature increase the yield of cross-linking increases. It is interesting to note that G(x) and $G(H_2)$ are changed symbatically.

In the case of the irradiation of polyethylene of high and low density at low temperatures and in a melt a significant difference was detected in the yield of gel fraction [125]. The analysis of these data made it possible for the authors of this work to assume that mainly amorphous sections of the polymer are subjected to cross-linking. The free radicals which were formed during the irradiation in crystalline ranges are captured by them, whereas the capture of radicals in polyethylene of low density is half as much as in polyethylene of high density, and cross-linking at 150°C is more effective in the first case than in the second. Polyethylene of both high and low density which is irradiated at a temperature of 25°C can be subjected to further cross-linking in the case of rapid heating to 150°C in an atmosphere of nitrogen. The summary effectiveness of cross-linking in this case is half as much as during the irradiation of the polymer directly in an amorphous state (at elevated temperatures).

The yield of *trans*-vinylene nonsaturation during irradiation also depends on temperature and increases in proportion to its increase.

In the work [113] it was shown that the number of double bonds of the vinylidene type formed depends on the temperature of the irradiated polymer. During the irradiation of isotactic polypropylene up to a dose of 200 Mrad at room temperature 2.5 times less vinylidene bonds are formed than at -196°C. The lesser accumulation of vinylidene nonsaturation at higher temperatures is attributed to the consumption of these double bonds for the interaction with free radicals.

It has been established [188] that the properties of polyethylene irradiated in a nuclear reactor depend strongly on the phase state of the polymer during irradiation. During irradiation in a melt (130-160°C) a rapid lowering is observed

in the melting temperature ($T_{пл}$) with an increase in the denseness of the network and a drop in the degree of crystallinity. During irradiation in a crystalline state (45-50°C) initially a weak lowering of $T_{пл}$ is observed, then its constancy and a certain increase; the degree of crystallinity drops with an increase in the denseness of the network considerably slower than during irradiation in a melt. The effects revealed can be explained by the different nature of the network which is formed in an amorphous and a crystalline polymer. In an amorphous polymer cross-linkages fix the erratic disposition of chains and facilitate a lowering in the degree of crystallinity and $T_{пл}$. Cross-links which are formed in crystalline polymer, along with a lowering of $T_{пл}$ and the degrees of crystallinity of the polymer, simultaneously increase $T_{пл}$ of the remaining crystals since they fix the local ordering of polymer chains.

In recent years a whole series of works has been published [189-192] on the clarification of the influence of phase state, temperature during irradiation, and the orientation of the polymer on the effectiveness of the cross-linking of a polyethylene of high density Marlex-50.

Thus in work [189]it has been shown that the temperature of a polymer during irradiation has a different influence on the effectiveness of cross-linking in the crystalline and amorphous areas. At moderate temperatures (25-90°C) cross-linking occurs more effectively in an amorphous state, at a temperature above 90-100°C cross-linking becomes more effective in a crystalline state. At 130°C the effectiveness of cross-linking in a crystalline state is two times higher than in a completely amorphous sample of the same molecular weight. Inhibited formation of the gel fraction in the crystalline areas in the case of irradiation at moderate temperatures is explained by the severe difficulties in the emergence of molecular bonds in a crystalline state, and also by the possibility of breaks in the chains. If

actually the formation of molecular bonds is inhibited due to insufficient mobility of links in the crystalline areas it is possible that the initial event of the interaction of radiation with the substance leads to the breaking of chains. The increase in the effectiveness of cross-linking by two times at temperatures higher than 90-100°C only in the crystalline areas is attributed to an increase in the mobility of links in ordered sections of the polymer and the related improvement in contact between the links of adjacent molecules. The expounded presentations have been confirmed by the data of work [190].

An attempt has also been undertaken [192] to explain the difference in the effectiveness of cross-linking in the crystalline and amorphous states by the fact that in a melt intramolecular contacts will be realized more and thus the probability of the flow of intramolecular cross-linking is greater than in the crystalline areas. Furthermore this difference can be conditioned by the fact that breaks in chains in amorphous and crystalline states occur with a differenct probability (the less tendency toward degradation in the crystalline state is connected with the cage effect, i.e., with the increased probability of recombination).

There are many works dealing with the study of the influence of the degree of crystallinity of polyethylene on the radiochemical yield of cross-linking, and analogous works dealing with other polymers [73, 98, 125, 190, 193]. In the majority of tests the irradiation dose was selected so that crystallinity would not disappear completely. For four forms of polyethylene of a various degree of crystallinity it was revealed [194] that the yield of cross-linking was the same (although according to other data [195] any physical processing of a polymer which leads to a decrease in the degree of crystallinity facilitates the formation of cross-linked structures).

According to work [196] the value of G(x) for isotactic polypropylene comprises 0.6 from the yield of cross-linking in

amorphous polypropylene. Investigations by the method of nuclear magnetic resonance [YaMR] (ЯМР) confirmed [197, 198] that cross-linkages in polypropylene are formed mainly in amorphous areas. In work [199] it was shown that the yield of cross-linking for amorphous polypropylene is equal to 0.8, and for isotatic - 0.2.

It is necessary to note that in the overwhelming majority of cases the changes in the degree of crystallinity of polymers (during the study of this factor on the yield of radiation cross-linking) are attained by a temperature shift or they compare data relating to polymers of different chemical structure. Neither approach ensures the isolation of the individual influence of each of these factors (separately - the degree of crystallinity and temperature). Therefore the interpretation of the available test data should be approached carefully.[1]

The study of the influence of orientation on the effectiveness of the cross-linking of polyethylene Marlex-50 is treated in work [191]; in it it is shown that at temperatures up to 70°C cross-linking flows more effectively in disoriented areas, in areas of 70-100°C such differences are not noted, but at temperatures above 100°C the effectiveness of cross-linking in oriented samples increases. Thus the effectiveness of the cross-linking of polymeric systems with oriented crystallites is lower than with disoriented (at moderate temperatures). However, with an increase in the mobility of molecular segments in the oriented samples with a temperature increase the retardation of the process of cross-linking is overcome.

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[1]The authors of this work have proposed a method which allows the realizing of various degrees of crystallinity of a polymer at the same temperature [R. P. Braginsky and others "High Molecular Compounds," IXA, 8, 1768 (1967)]. The utilization of this method makes it possible to exclude the general deficiencies inherent to works dedicated to the development of the influence of crystallinity of cross-linking processes.

The question of an increase in the effectiveness of radiation cross-linking of polyethylene by irradiation at elevated temperatures has been reflected in the patent literature [200-203].

The Influence of Supramolecular Structure

In the works [171, 204] the process of the radiation cross-linking of blocks and monocrystals of polyethylene of high density has been illuminated and the following differences uncovered: in a block and a fine film a greater tendency toward cross-linking is noted than in a monocrystal or thicker film. These differences assign the best contacts between the folding surface of individual lamellae in fine films and blocks. The processes which lead to an improvement in contact increase gel formation. It has been also established [96] that during the irradiation of polyethylene three times more hydrogen is liberated from the block than from the monocrystal. The authors of this work assumed the possibility of intramolecular cross-linking of monocrystal consisting of lamellae - layers of routinely constructed molecules. Intramolecular cross-linkages do not influence the content of the gel formation in irradiated polymer and do not participate in the formation of cross-linking.

A detailed study of the influence of the conditions of crystallization on radiation cross-linking of polyethylene is made in works [127, 128, 130, 202, 205]. Thus in works [127, 205] it is shown that cross-linking occurs most effectively in a block. Apparently the different content of gel fraction in irradiated samples of polyethylene which were crystallized under different conditions is connected not with differences in the overall content of cross-linkages formed during irradiation up to an identical dose, but with the different relationship of intermolecular and intramolecular bonds which do not influence the solubility of the polymer. For the purpose of studying the influence of the packing of lamellae in a monocrystal of polyethylene

on radiation cross-linking [128] a polymer was systematically loosened and dispersed with the help of ultrasound; as a result the content of insoluble fraction formed during the irradiation was strongly diminished, hence it follows that gel formation is conditioned completely by the aggregation of lamellae, and the cross intermolecular bonds which participate in the creation of the steric network are formed between the lamellae.

On the basis of a through study of the influence of the conditions of crystallization and annealing on the process of gel formation in irradiated polyethylene [128-130, 205] a concept was formed about the fact the cross-linking of polyethylene occurs mainly in the sites of folds and bends of chains, whereas the initial folds are retained even in cross-linked systems. Cross-linking occurs mainly between the molecules of two layers arranged in series. In the case when intramolecular bonds are formed between the folds of the belt [206] (formed by one molecule) or multiple cross-linkages (the connection between already cross-linked molecules), the content of gel fraction in the polymer during irradiation does not increase. With the formation of such a type of bonds near the folds in the structure of the polymer there is the possibility of the appearance of large or small rings, depending on the localization of these bonds inside one belt or between two adjacent ones. More probable is the formation of small four- or five-member rings (the existence of such rings is predicted in work [95] on the basis of spectral data). Such a mechanism for the formation of rings increases the defectiveness of the polymer crystal. The authors of this work consider that such a deviation of the mechanism of cross-linking from random law, the determined selectivity of the process of cross-linking (cross-linking flows mainly in the sites of folds), is extended not only to intramolecular, but also to the intermolecular cross-linkages which are formed during the irradiation of crystalline polymers.

The results of a relatively small quantity of works on the radiation cross-linking of polypropylene attest to the fact that the quantity of cross-linkages strongly influences the atactic level of this polymer: the higher the atactic level the higher the degree of cross-linking.

As a whole it is necessary to note that the presentations expounded above reflect to a considerable extent the subjective point of view of the authors of the quoted works, and their contradictoriness is conditioned by the absence of a completed concept about the structure of polymers.

The Influence of Molecular Weight and Distribution by Molecular Weights

The initial molecular weight and molecular weight distribution not only are expressed in many initial properties of polyolefins, but also to a known degree predetermine the properties of these polymers after irradiation. In this connection they studied the influence of the initial molecular weight on the process of radiation cross-linking of polyethylene [123, 207, 208].

A comparison was made of irradiated polyethylenes of low density (molecular weight from 7000 to 25,000) with Alcowax (molecular weight 2100) and paraffin wax (molecular weight 480) and for each sample they determined the minimal dose in which a sample (strip) retains its form during swelling in toluene at a temperature of 90°C [78]. It was established that the irradiation dose required for the formation of cross-linking in the polymer depends on its initial molecular weight. Thus for the creation of such a structure in paraffin wax a dose of $(8\text{-}9)\cdot 10^8$ rad is required, whereas for polyethylene it is almost 100 times less.

The dependence was obtained experimentally of the initial molecular weight on the dose necessary for the transformation of paraffins with a chain length from C_7 up to C_{36} into stagnant

at 200°C; the greater the molecular weight of paraffin the lower the irradiation dose necessary for the formation of an infinite network [208].

So the dependence was obtained for gel fractions of ten various types of branched polyethylene on the initial value of molecular weight [207]. Analytically it can be expressed by the formula

$$r \cdot M_{w_0} = 8{,}06 \cdot 10^5,$$

where M_{w_0} - the initial weight-average molecular weight, and r - the dose of gel formation (gel point). It is evident that the higher the initial molecular weight, the lower the doses necessary for obtaining a cross-linked structure.

As shown in the works [208, 209], the value of the gel fraction at the assigned irradiation dose of polyethylene depends on the molecular weight distribution. The fundamental regularity consists of the fact that for obtaining an identical content of gel fraction polymers with a wide molecular weight distribution have to be irradiated to higher doses than with narrow.

THE INFLUENCE OF ADDITIVES

In the preceding sections we examined the fundamental processes taking place in polymers during irradiation, and also the reaction mechanisms of the initial materials of radiolysis with each other and with the molecules of the surrounding substance, the influence of the medium, in which the polymer is irradiated, its temperature, phase state, the degree of crystallinity, and other peculiarities.

In the light of the examined presentations it is completely evident that the introduction into the individual polymer of any additive can considerably influence the changes which take place in the material under the action of ionizing radiations and after

it, depending on the interaction of additives with the reactive or excited products which are formed in the polymer during irradiation [210].

Stemming from the general nature of participation in the processes which proceed under the action of ionizing radiations, such additives and the low-molecular components of the material, for example plastifiers, can be divided into two fundamental categories: the active and the inert substances. Active additive in turn can be divided into two classes: the substances which absorb the radiant energy preceived directly by the polymer (i.e., disproportional to their molar fraction taking electron density into account) and substances which enter into a chemical interaction with the reactive products which are formed during irradiation. Inert additives (amplifying agents or fillers) participate in radiation processes because they are a component part of the entire mass of the product in which the radiant energy is scattered and absorbed. If the content of such a filler makes up a noticeable part of the weight of product, then the filler will absorb a significant fraction of the radiant energy and therefore reduce or increase radiation effects in the irradiated product, depending on its own radiation stability.

Based on application additives introduced into polymers can be classified in the following manner: 1) amplifying agents or fillers; 2) substances which reduce the degree of chemical and physical changes which take place in a polymer during irradiation, i.e., raising its radiation stability - the so-called antirads; 3) substances which inhibit the process of oxidation of polymer both during irradiation and during the subsequent exploitation in the air at increased temperatures - anatioxidants or thermostabilizers; 4) substances which promote (facilitating the onset) specific chemical changes which flow in a polymer during irradiation - the so called sensitizers.

Active Fillers

Amplifying agents, or active fillers, are used frequently in industry since they make it possible to improve the physico-mechanical properties of a product, to reduce the expenditure of the fundamental polymeric material, and therefore to reduce the price of the product. If as the filler a material which possesses higher radiation stability than the polymer itself is used, then, as a rule, such a filler only diminishes the radiation changes in the polymer - filler system because the fraction of the absorbed energy necessary for the polymer diminishes. Such fillers include various carbonic blacks, silicon dioxide, glass fiber, talc, and others. For instance, for the improvement in the mechanical properties of irradiated polyethylene, and also increasing it resistance to the action of oxygen and ultraviolet irradiation into the stabilized polyethylene prior to irradiation mineral fillers (soot, SiO_2) are introduced to the extent of 25-100 parts by weight to 100 parts by weight of polymer [211]. After irradiation the polyethylene with the filler possesses higher strength than polyethylene without the filler [212]. The difference in strength characteristics is expressed especially sharply at eleveted temperatures (Table 10).

Table 10. The influence of filler on the strength characteristics of irradiated polyethylene at various temperatures.

Polyethylene	Breaking strength, kg/cm^2		
	20 °C	100 °C	150 °C
Without filler	182	35	7,5
With filler	171	63	33

An analogous effect was obtained not only on polyethylene, but also on other polyolefins, especially on the copolymer of ethylene with propylene (propylene content 7 mole %) [213]. Prior to irradiation the chlorides of bivalent tin, bi- and trivalent iron

were introduced into the polyolefin to the extent of 10 parts by wt. they were irradiated up to a dose of 100 Mrad. The strength characteristics of such a material at various temperatures are given in Table 11.

Table 11. The Influence of metal chloride on the strength characteristics of polyethylene at various temperatures.

Material	Temperature of testing, °C	Breaking strength, kg/cm²		Relative elongation, %	
		prior to irradiation	after irradiation	prior to irradiation	after irradiation
Polyethylene of low density	20	117	115	500	100
	150	-	5.5	-	90
	200	-	0	-	-
The same + $SnCl_2 \cdot H_2O$	20	135	123	310	160
	150	-	13	-	85
	200	-	9.6	-	32
The same + $FeCl_2 \cdot H_2O$	20	106	124	160	97
	150	-	9.4	-	65
	200	-	7.2	-	45
The same + $FeCl_3 \cdot nH_2O$	20	105	139	150	70
	150	-	9.3	-	70
	200	-	6.0	-	40

For the purpose of increasing the impact elasticity of polyethylene compositions were prepared which contained 10-30% of filler - calcium silicate, alumina or aluminum silicate and others and 0.5-15% vinyl triethoxysilane, and then they were irradiated by the usual method [211].

It has also been established that plastomers on the basis of glass fiber and epoxies (as also for other heat-reactive resins) possess greater radiation stability than the resin itself [214, 215].

Antirads. Radiation Protection

Various chemical groups differ strongly from one another in sensitivity to irradiation, however, their susceptibility is a very relative value, it can change strongly because of the presence of other groups in the same or in adjacent molecules. In cases when the effect amounts to the lowering in the reactivity of the basic component of the system due to the presence of another component or additive, it has been accepted to speak about radiation protection. The increase in the reaction activity of the basic component as a result of the presence of another component or additive corresponds to the effect of radiation sensitization.

The questions of radiation protection are extremely important when using materials in the active zone of ionizing radiations.

Based on the principle of action of a protective additive the processes of protection can be divided into two basic groups. The first group includes the processes of actual protection, in this case the protective additive absorbs energy from the fundamental irradiated substance (protection of the "sponge") and it scatters this energy in the form of heat or light, whereas the additive itself barely undergoes any irreversible chemical changes (protection is called internal if the chemical groups which transform the radiant energy into other forms of energy without a change in their own structure have been built in directly into the molecule of the protected polymer, and external - if they are simply distributed in the bulk of the polymer in the form of an additive).

Good protective additive for many chemical compounds are aromatic hydrocarbons, since they have a large number of low lying excited states, possess the low ionizing potentials, and themselves are radiation resistant. The transfer of energy from the higher excited states of the main compound or charge transfer with an ion of the main compound gives rise to the scattering of

power in an aromatic hydrocarbon. This scattering is accomplished as a result of fluorescence or heat evolution and is accompanied by insignificant decomposition of the aromatic compound itself.

Thus in works [216, 217] it is shown that small quantities of benzene protect cyclohexane from decomposition during irradiation, whereupon this protection is the result of the transfer of ionization and excitation from cyclohexane to benzene.

It has been established that the radiation stability of polyethylene can be raised by mixing it with compounds for which resonance stabilization is characteristic - naphthalene, anthracene, phenanthrene (external protection), or by inoculating polyethylene with styrene (internal protection) [218]. A graft copolymer of styrene and polyethylene possesses better radiation stability than a mixture of polystyrene and polyethylene. Apparently the transfer of energy inside the molecule is accomplished more readily than between molecules, when a major role already can be played by the relative mobility of active chemical groups. Such an internal protection was observed during the irradiation of linear paraffins with a known number of carbon atoms in a chain, in the molecules of which naphthyl groups were connected in various positions along the alkyl chain [219]. In this same work it was shown that the area of the protection of every aromatic grouping is disseminated along the chain to a distance of approximately 4-6 carbon atoms.

An antirad action on polymers is exerted by many aromatic amines: di-β-naphthyl-n-phenylenediamine, phenyl-α-naphthylamine, etc. In the work [219] it is shown that in a very small concentration of these substances in polyethylene (0.2-0.5%) the yield of cross-linking is considerably reduced.

The mechanism of the protective action of aromatic amines during radiolysis of polymers has been studied in work [220] it

is shown that their protective action is accomplished in the preradical stage of radiolysis, i.e., it is connected with the processes of transfer of the energy of excitation or an electron. Ion-radicals of amines are formed during the transmission of energy absorbed by the polymer to the amine, as a result of which its ionization occurs.

In work [221] it is shown that many industrial antioxidants - aromatic amines and phenols - not only are inhibitors of oxidation during the thermal aging of irradiated polyethylene, but also antirads, especially in the area of the small irradiation dose [222]. The effectiveness of their protective action with respect to the reaction of radiation cross-linking depends on the additive concentration, the compatibility of the additive with the polymer, the melting point of the additive, and others.

Strong antirads have been revealed for polypropylene, for example ionol [223, 224]. A very high effectiveness of protective action on polypropylene is possessed by diatomic phenols containing hydroxyl groups in *ortho*-positions, for example pyrocatechin [225].

Another mechanism for protection is known by the name of protection of the "sacrifice" type. In this case the additive, while carrying out the protection of the main compound, suffers irreversible chemical changes and is destroyed. The summary radiation damage in the system remains approximately the same as it was before the introduction of the additive. Examples of protective additives of the "sacrifice" type are iodine and other acceptors of free radicals [226]. With the use of such compounds the possibility of reactions of free radicals formed in the initial event with the molecules of polymer is averted. A strong protective action during the radiolysis of polyethylene is exerted by small additives of S, Se, and Te [227].

It is assumed [14], that radiation protection with the help of additives can be accomplished by several mechanisms.

1. By the transfer of energy from the polymer to the protective additive without chemical changes in it. The additive can scatter this energy, not having suffered any irreversible chemical changed, or be changes and lose the protective activity. In the latter case protective action will be discontinued when all the additive will be destroyed or changed.

2. By the reduction of damages induced by radiation, with the participation of additive which itself can be changed or not be changed.

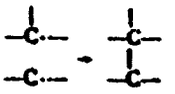
If the main reaction in the polymer during the influence of radiation is the loss of hydrogen with the formation of the polymeric radical R·, then protection can be reduced to the transfer of a hydrogen atom from the additive (AH) to this radical and the formation of a low-activity radical:

$$RH \longrightarrow R\cdot + H. \qquad (101)$$

$$AH + R\cdot \longrightarrow A\cdot + RH. \qquad (102)$$

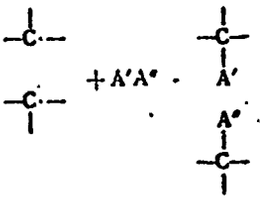
If as a result of ionization an electron is torn from the polymer molecule the additive can supply this molecule with the missing electron, remaining sufficiently stable itself and without participating in other reactions, until it captures another electron.

If one assumes that cross-linking occurs during the interaction of two polymer radicals



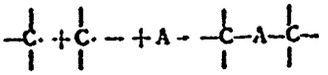
(103)

then the molecules of the additive can be joined with the radicals with the formation of stable side groups or less active radicals, i.e.,



(104)

In the case of degradation which flows by means of breaks in the main chain the protective additive can connect between itself two polymer radicals (to interlace the ruptured chain) and thus "heal" the damage caused by radiation. Here the average molecular weight is not noticeably changed



(105)

In many similar cases strictly protection against chemical changes induced by radiation is absent, but the changes taking place acquire another nature and are converted into such which do not influence the properties which are critical in the given concrete case.

3. The addition can react with radical formed during irradiation earlier than the latter will be able to attack and modify the polymer. For instance, during irradiation in the presence of oxygen the additive can react with free radicals and avert the formation of unstable peroxides in the polymer molecule; otherwise these peroxides could lead to degradation.

The three mechanisms of protection enumerated can be considered as: 1) the removal of absorbed energy before chemical changes occur; 2) the inactivation of chemical formations, for example the radicals which were formed during irradiation; 3) the protection of the polymer molecule from active formations which arose outside it.

Quantitatively it is accepted to characterize the effectiveness of the protective action of additives by the protection factor and by the factor of energy transfer.

If we designate by r_0 the irradiation dose necessary for obtaining specific changes in the absence of additives and through r_p the corresponding dose when there is a protective additive, then the measure of the decrease in the effect of radiation is equal to r_0/r_p, and the portion of lost energy as a result of the presence of the additive is equal to $1 - \frac{r_0}{r_p}$. This value is called the coefficient of protection. The factor of energy transfer expresses the portion of the energy diverted to additive divided by the concentration of additive.

In Table 12 data are given [228] on the protective action of various additives on polyethylene.

Table 12. The protective action of additives on Polyethylene.

Sample of polyethylene	Content of additive part by weight	Dose at which 90% gel content is attained	Coefficient of protection	Factor of energy transfer
Without additives	-	100	0	-
With dibutyltin maleate	5	220	0.58	12.0
With β-naphthol	5	250	0.60	12.6
With dinaphthyl methane	5	300	0.66	13.7

Let us examine the course of the computation of the coefficient of protection and factor of energy transfer in the example of dinaphthyl methane. With a content of 5 parts by weight of it a 90%-content of gel fraction in polyethylene is reached with a dose of 300 Mrad (instead of 100 Mrad for pure polyethylene). Therefore the coefficient of protection $1 - \frac{r_0}{r_p} = 1 - \frac{100}{300} = 0.66$. Therefore in the presence of dinaphthyl methane only 34% of energy which is necessary for every polymer molecule causes chemical changes (the effect in the absence of additive is accepted as 100%). Since the quantity of polymer comprises only 95% by weight, the energy utilized for the realization of chemical

changes observed during irradiation comprises 0.95·0.34 = 0.32 or 32%, and 68% is taken off in this or that form as the result of the action of additive. The quantity of additive comprises 5 parts by weight. If the primary energy absorption of radiation occurs according to random law, then protection increases the effective energy absorption by the molecules of the additive by 68:5 = 13.7 times.

The mechanism of the transfer of energy to the molecules of additive is not conclusively clarified and it is the subject of further investigations.

Heat Stabilizers. Protection from Oxidation

The influence of oxygen on polymers during and after irradiation, and also the mechanism of radiation oxidation were examined above. At the same time one ought to keep in mind that polymers are very susceptible to oxidation, especially at elevated temperatures, and therefore as a rule a certain quantity of stabilizers are introduced into them for the prevention of oxidation of the material during its technical processing into a product (such treatment is usually conducted at elevated temperatures, in any case exceeding the softening temperature, and sometimes even the melting point of the polymer).

Irradiated polyolefins, as it will be shown, can be exploited at temperatures which considerably exceed the softening temperature and even the melting point of the corresponding polyolefins in the nonirradiated form. Since with a temperature increase the intensity of the oxidation process substantially increases, and the properties of material during aging at elevated temperatures rapidly deteriorate, the question of the thermal stabilization of such radiation-modified polyolefins is especially urgent, because only the effective protection of an irradiated polymer from

oxidation makes it possible to realize all its valuable properties for a prolonged time.[1]

The study of the oxidation of hydrocarbons both in the liquid and solid phase, and also the mechanisms of thermal stabilization have been treated in many works and detailed monographs have been published [229-232].

In principle the fundamental scheme of the process of thermal oxidation of polymers is analogous to that already examined in the section dealing with radiation oxidation, however, there is a certain peculiarity: during thermal oxidation the process is initiated by the interaction of hydrocarbon with molecular oxygen, whereas during the irradiation free radicals are accumulated basically as a result of the processes of ionization and excitation under the influence of radiation.

Let us examine the sequence of reactions during the oxidation of polyolefins more comprehensively.

It is known [232] that the oxidation of polymers is a chain process which flows with the participation of free radicals which can be formed during the interaction of two valence-saturated molecules

$$RH + O_2 \rightarrow R\cdot + HO_2\cdot, \quad E = 25-30 \text{ Cal.} \qquad (106)$$
(low-activity radical)

Initiation in this scheme in polymers is very probable since their oxidation frequently begins already at 100°C. Polymer macroradicals react with oxygen, forming peroxiradicals

[1]In this case we are speaking of the exploitation of the polymer in the presence of atmospheric oxygen. If we examine exploitation in a deep vacuum or an atmosphere of neutral gas the necessity for the thermal stabilization of the polymer remains, but only for the period of its processing into a product, if this processing is conducted in the air and at increased temperatures.

$$R\cdot + O_2 \rightarrow RO_2\cdot, \quad E = 0 \text{ Cal.} \qquad (107)$$
(more stable radical)

Although the $RO_2\cdot$ radical possesses less reactivity than $R\cdot$ it nevertheless can break away an atom of hydrogen from organic compounds and be converted into hydroperoxide. In this case the radical $R'\cdot$ is again formed and is able to continue the chain

$$RO_2\cdot + R'H \rightarrow R'\cdot + ROOH, \quad E \doteq 4{,}5 \text{ Cal.} \qquad (108)$$

Concentration $[R\cdot] \ll [RO_2\cdot]$. During oxidation the chain breaks as a result of the recombination of $RO\cdot_2^!$ peroxide radicals and is accompanied by the formation of peroxides and molecular oxygen

$$RO_2\cdot + RO_2\cdot \rightarrow ROOR + O_2. \qquad (109)$$

The hydroperoxides which are accumulated during the oxidation of a polymer decompose into active alkoxyl and hydroxyl radicals, i.e., the number of active centers increases

$$ROOH \rightarrow RO\cdot + HO\cdot, \quad E = 20 \text{ Cal.} \qquad (110)$$

The radicals formed during the decomposition of hydroperoxide can then participate in the reactions

$$RO\cdot + R'H \rightarrow ROH + R'\cdot, \qquad (111)$$
$$HO\cdot + R'H \rightarrow H_2O + R'\cdot. \qquad (112)$$

Furthermore, present test data [233] indicate that hydroperoxide decomposes during reaction with a polymer according to the equation

$$ROOH + RH \rightarrow RO\cdot + H_2O + R\cdot. \qquad (113)$$

Hydroperoxide would decompose still more rapidly if it reacted with a compound in which the binding energy of the hydrogen atom would be less than in RH.[1]

[1]As the antioxidants of polymers they frequently use aromatic amines. It is known that the binding energy N-H in such antioxidants is considerably less than the binding energy C-H in hydrocarbons, and this gives rise to undesirable consequences, especially, to the initiation of oxidation with an antioxidants themselves.

The rate of the consumption of hydrocarbon in the chain reaction of oxidation is expressed by the following equation:

$$\frac{d[RH]}{dt} = K_2[RO_2\cdot][RH]. \qquad (114)$$

Since concentration [RH] is practically constant the rate of the consumption of hydrocarbon d[RH]/dt depends only on the concentration of $[RO_2\cdot]$. In turn the concentration of $[RO_2^{\cdot}]$ is determined by the relationship of the rates of formation and disappearance of free radicals.

It is assumed that the role of antioxidants (or inhibitors (IH)) is reduced to the fact that they react with active RO_2 radicals, as a result of which inactive products are formed

$$ROO\cdot + IH \rightarrow I\cdot + \text{inactive products}. \qquad (115)$$

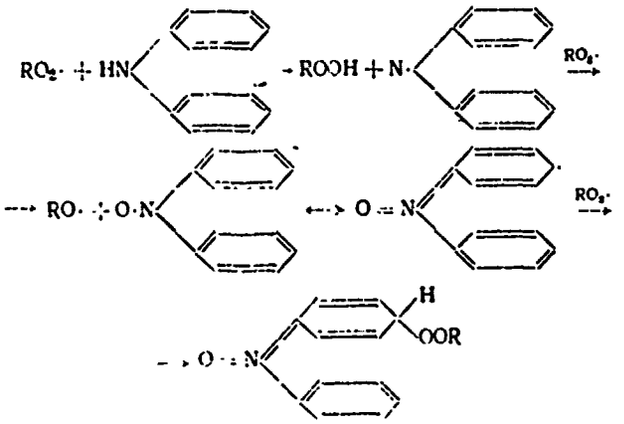
The most widespread antioxidants of polyolefins are aromatic amines and phenols (PhOH).

The chemical action of antioxidants during the thermal aging of polyolefins consists of the capacity to break reaction chains during the interaction with $RO_2^{\cdot}$ radicals [234]

$$PhOH + RO_2\cdot \rightarrow RO_2H + PhO\cdot . \qquad (116)$$

As a result of this reaction instead of the active radical $RO_2^{\cdot}$ the low-activity phenoxyl radical PhO· is formed. It is not able to continue the chain reaction. This radical attaches to itself the peroxide radical, breaking one additional reaction chain and converting into quinone.

Aromatic amines also interact with two $RO_2^{\cdot}$ radicals;



(117)

The formation of phenoxyl and nitroxyl radicals during the inhibition of the thermal-oxidative degradation of polymers is proved by the [EPR] (ЭПР) method [235]; quinones have been isolated by a series of the researchers [236].

As the basis for the generally accepted scheme for the inhibition of oxidation two assumptions have been taken: 1) the inhibitor breaks the chains of the reaction, but it does not influence the process of the germination of oxidation chains; 2) hydroperoxide decomposes with the formation of two active free radicals. From these assumptions it follows that the rate of consumption of inhibitor is equal to the rate of initiation and the induction period (i.e., the time during which the autocatalytic reaction of oxidation is not developed) increases proportionally to inhibitor concentration in polymer.

However, experimental investigations showed [237] that antioxidants are expended approximately according to linear law up to the moment of the lowering in their concentration to critical, whereupon they rapidly disappear, but the induction period with an increase of inhibitor concentration does not increase linearly but more slowly. These data attest to the complex mechanism of action of antioxidants and make it possible to assume that the latter not only break the reaction chains, but can also

initiate oxidation. Actually if the antioxidant only breaks chains, then its introduction into a polymer cannot lead to the recudtion of the induction period; if it possesses the capacity both to break and to initiate chains, then under some conditions the addition of it can lead to a reduction in the induction period.

Three probable mechanisms are suggested for the initiation of oxidation by antioxidants.

1. The oxidation of the inhibitor according to the reaction

$$IH + O_2 \rightarrow HO_2\cdot + I\cdot . \qquad (118)$$

In this case a comparatively active radical HO_2 is formed, the presence of which during oxidation is proven in work [238].

2. The low-activity radicals of the inhibitor I can enter into a reaction with the molecules of the polymer

$$I\cdot + RH \rightarrow IH + R\cdot . \qquad (119)$$

In this case active radicals are formed [239].

3. Antioxidants can initiate oxidation by reacting with hydroperoxide according to the arrangement [240]

$$ROOH + IH \rightarrow RO\cdot + H_2O + I\cdot . \qquad (120)$$

In the light of the presentations expounded about the dual function being fulfilled by the inhibitors of oxidation in a polymer (the breaking of chains and the initiation of oxidation) it becomes understandable why in a number of cases the joint use of two antioxidants gives a considerably stronger effect of protection of a polymer than should be expected, stemming from the summary effectiveness of each of them individually (so called

synergistic effect, i.e., their nonadditive contribution with joint use). The phenomenon of synergism - the mutual strengthening of the action of antioxidants - is examined comprehensively in a number of works [239, 241-243]. The chemical mechanism of this phenomenon is manifested in cases when the radical of the inhibitor causes the initiation of oxidation, and the additive of the second substance captures these radicals.

Thus the fact that antioxidants along with breaking the chain participate in the initiation of oxidation is completely negative. Here the major role is played by the formation of hydroperoxide during the interaction of $RO_2\cdot$ peroxide radicals with the antioxidants, the molecules of which contain a weakly bound atom of hydrogen (related to them are practically all the widely used derivatives of phenols and aromatic amines).

All the presentations expounded above relative to the mechanisms of oxidation and stabilization of polymers are also applicable to irradiated polymers; however in the latter case there are some characteristic properties connected both with the course of the oxidation process and with the mechanism of thermal stabilization. These peculiarities, which are noted in a number of works, are conditioned by two causes: 1) by the presence in irradiated polyolefins of a significant quantity of tertiary atoms of carbon accumulated during radiation cross-linking, and 2) by the possibility of the expolitation of irradiated polyolefins at temperatures which exceed the melting point.

The classical approach to the study of thermal oxidation is reduced to the determination of the induction period, the study of the kinetics of accumulation, and analysis and identification of the oxidation product both in the pure polymer and in the presence of an anticxidant. In this case it is assumed that the reaction mechanism at temperatures which exceed the melting point of polymers is not substantially changed, but only the reaction rate increases.

At the same time some investigation [244, 245] focused attention on the individual specific peculiarities of thermal oxidation of radiation-cross-linked polymers.

An investigation was made [246] of heat aging of polyethylene of low density, both pure and heat-stabilized by special additives after irradiation by γ-radiation in an inert atmosphere up to various doses, by methods of extraction (gel fraction), swelling in the vapors of organic solvents at room temperature, infrared spectrometry, and also by the determination of strength characteristics. The content of nonsaturation (vinylene in irradiated and vinyl and vinylidene in nonirradiated samples) was varied with the help of chlorination, and the influence of the free radicals accumulated during irradiation on the process of thermal aging was eliminated by means of the annealing of samples in a neutral medium.

Figures 7-9 show the dependences of the relative change in content of the gel fraction and also the strength characteristics of polyethylene (pure and heat-stabilized) on the duration of aging in the air at various irradiation doses and temperatures. Attention is focused on the nonmonotonic course of the change in relative content of gel fraction with an increase in the duration of aging, and also the correlation between times corresponding to the minimum of this curve and to the total losses of strength of the polymer at each of the testing temperatures. The sharp lowering in the content of the gel fraction during the initial period of aging attests to the intensively flowing process of thermal oxidation polymer degradation; a subsequent increase in the content of the gel fraction is apparently conditioned by the process of structuration, however, it is not accompanied by an improvement in mechanical characteristic. In heat-stabilized polyethylene the course of the change in this dependence is observed, but the relative value of extreme is less, and with an increase in the time of aging the content of the gel fraction increases nomotonically, approaching the limiting value.

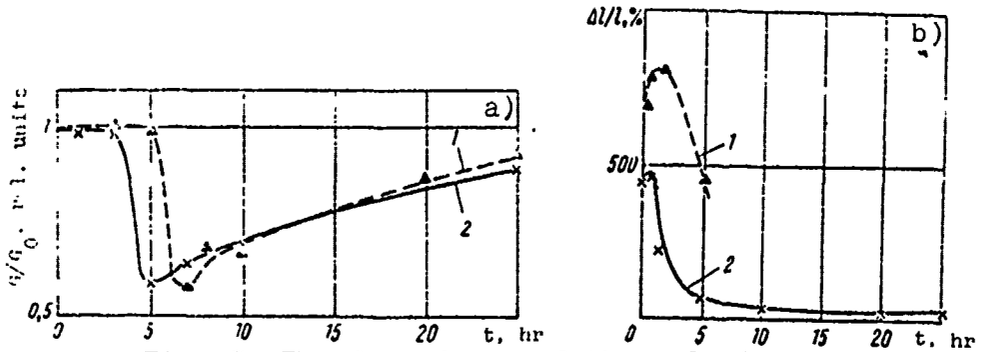


Fig. 7. The dependence of the relative content of gel fraction a) and the relative elongation b) of irradiated polyethylene of low density on the time of aging t at 175°C: 1 - irradiation dose 50 Mrad; 2 - irradiation dose 100 Mrad.

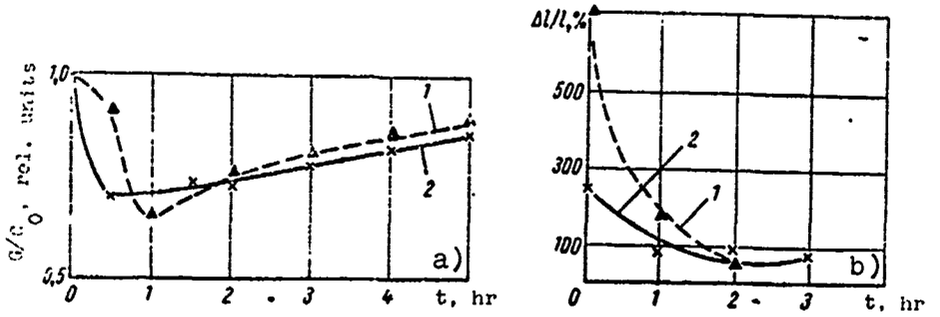


Fig. 8. The same at 200°C.

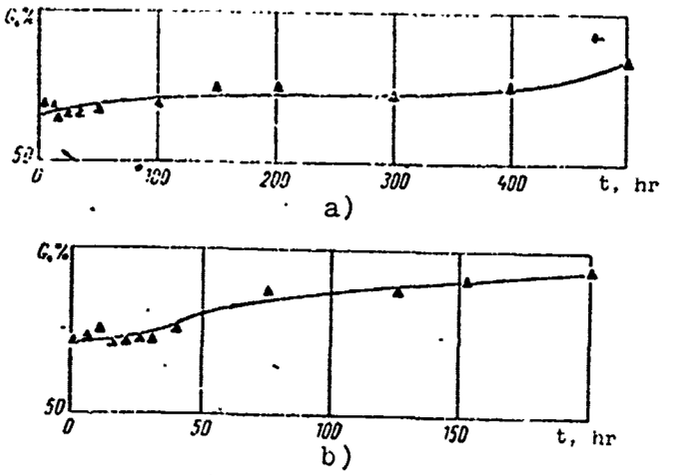


Fig. 9. Dependence of the content of gel fraction of heat-stabilized polyethylene irradiated up to 100 Mrad on aging time t at 175°C a) and 200°C b).

The analysis of the given curves shows that with an increase in the irradiation dose the time of achievement of minimum diminishes, but with an equal irradiation dose this time is less, the higher the aging temperature. With the same aging temperature independent of the irradiation dose the processes of structuration flow at a constant rate.

Figure 10 shows the dependence of the coefficient of swelling of the gel fraction (K_g) of irradiated polyethylene in xylol at 25°C after aging at 200°C in air; the calculation is accomplished on the assumption that the coefficient of swelling of the gel fraction during aging is not changed. It is evident that during aging value of K_g increases sharply, and then, having achieved a value characteristic for nonirradiated polyethylene, continues to increase slowly. The time interval which corresponds to a sharp change in K_g is approximately equal to the time of onset of the minimum on curve in Fig. 8a. The rapid increase of K_g during the initial period of aging is conditioned by the breaking of the cross-linkages C–C which were formed during irradiation (the fall in the content of gel fraction corresponds to this). The subsequent slow increase of K_g is connected with structuration (the increase in the content of gel fraction), however, the oxygen-containing cross-linkages being formed loosen the structure of the polymer, thus increasing the volume of intermolecular voids.

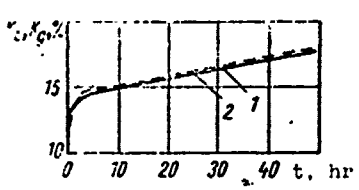


Fig. 10. The dependence of the coefficient of swelling of polyethylene irradiated in a dose of 100 Mrad on the time of aging t at 200°C: 1 – the coefficient of swelling of irradiated polyethylene (K_0); 2 – the coefficient of swelling of the gel fraction of irradiated polyethylene (K_g).

Spectroscopic studies showed (Fig. 11) that with an increase of temperature and time of annealing the rate of the subsequent thermal oxidation is lowered both for pure and for heat-stabilized polyethylene. The study of samples with a various initial degree of unsaturation showed that the absolute increase of oxygen-containing groupings in all cases is approximately identical, but the content of double bonds during aging did not substantially change.

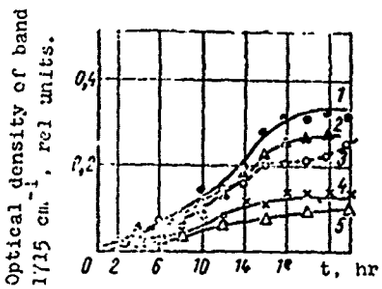


Fig. 11. Change in the relative concentration of carbonyl groups during thermal oxidation aging of polyethylene irradiated up to 100 Mrad: 1 - polyethylene heat-stabilized without annealing and pure polyethylene, annealing at 150°C, 3 hr; 2 - pure polyethyelene annealing at 100°C, 30 min; 3 - the same, annealing at 200°C, 30 min; 4 - the same, annealing at 150°C, 3 hr; 5 - the same, annealing at 200°C, 3 hr.

The examination of the totality of test data obtained shows that the process of thermal oxidation of irradiated polyethylene at temperatures higher than the melting point flows according to a mechanism which is substantially different from that generally accepted for nonirradiated polyolefins in the area of lesser temperatures.

The nonmonotonic course of the dependence of the content of gel fraction on the duration of aging is conditioned, as already mentioned above, by the simultaneous flow of two fundamental competing processes: the thermal oxidation degradation which is developed by the usual mechanism with the formation of peroxide and hydroperoxide radicals, and structuration. Under normal conditions the peroxide radical being formed recombines with the polymer radical with the formation of a peroxide cross bridge. However, at temperatures above 150°C such peroxide bonds are destroyed.

The drop observed in the content of gel fraction during the initial period of aging in the light of the described mechanism can be explained only by the fact that the process of oxidation of irradiated polyethylene flows selectively with the participation of tertiary atoms of carbon in the C—C cross-linkages which were formed during irradiation. This is confirmed by the fact that the yield of degradation during the initial period of aging is proportional to the irradiation dose, i.e., the density of cross-linkages. The subsequent increase in the content of gel fraction attests to the structuration of the polymer. The cross-linkages being formed are oxygen-containing - this stems from a comparison of the content of gel fraction in pure and heat-stabilized polyethylene, on the one hand, and from the correlation of this process with an increase in the concentration of bound oxygen - on the other.

The constancy of the relative value of extremes makes it possible to assume that the formation of these oxygen-containing bonds is a process determined by formation and decomposition of peroxide bridges. The presence of bend on the ascending branch of the curve confirms this assumption, because these processes flow simultaneously, and the somewhat lower rate of the second process predetermines its course for a certain period of time after the conclusion of the first process.

The subsequent slower process of structuration, which flows with the participation of oxygen, is apparently conditioned by the cross-linkages as a result of the interaction of the polymer macroradicals which arose during the breaking of chemical bonds of the tertiary atoms of carbon and other weak places of the polymer chain. Available data make it possible to assume that the process of structuration is conditioned by the formation of simple ether bonds.

The proposed mechanism for thermal oxidation aging makes it possible to explain the data obtained earlier [244, 245] on the lesser thermal resistance of irradiated polymers as compared with nonirradiated, and also to stress the importance of the solution to the problem of heat stabilization of irradiated polymers for the creation of the possibility for the realization of their potentially valuable properties.

In works by the authors the question of the possibility of a thermal stabilization of irradiated polyethylene and other polyolefins has been studied in detail, for example, the copolymer of ethylene with propylene. Formulas for effective heat-stabilized systems have been developed, the defficiency of thermal stabilization of irradiated polyolefins has been investigated over a wide range of temperatures (the properties of heat-stabilized irradiated polyethylene are examined in the following chapter), the peculiarities of the mechansim of the synergistic action of stabilizing systems have been revealed, and, along with chemical, the structural mechanism for the stabilization of irradiated polymers has been disclosed.

The testing of different types of compounds as antioxidant additives showed [234, 247, 248] that certain organo-tin and also other compounds exert a stabilizing action on the process of thermal aging of irradiated polyethylene. The introduction of these heat stabilizers to the extent of up to 5-7 parts by weight to 100 parts by weight of polymer makes it possible to increase the duration of utilization of irradiated polyethylene in air up to the loss of elasticity (relative elongation is reduced to 100%) as compared with the irradiated polyethylene not containing special additives at a temperature of 150°C from 150-200 to 1500-2000 hr, and at 200°C - from 10 to 50-60 hr.

Further studies showed [249] that the effect of thermal stabilization of irradiated polyethylene can be substantially

strengthened, if as stabilizers individual substances are not used, but their specially selected mixtures with a specific relationship of components. In this case a clearly expressed synergistic effect is observed [250]. The use of combined synergistically interacting additives as heat stabilizers of irradiated polyethylene ensures the effective protection of this material from oxidation in air at a temperature of 150°C for 5000-6000 hr, and at 200°C - for 150-200 hr and more.

By the utilization of methods of infrared spectrometry and extraction [251], by the study of Mossbauer's effect [252], the analysis of the strength and thermomechanical characteristics of a material during thermal aging [253], and also by using other physicochemical methods of investigation the influence of the thermal aging of irradiated polyolefins was revealed. Specifically it has been established that additives are expended both during radiation and thermal influences, that the majority of the stabilizing systems along with an antioxidant action play the roles of antirads.

The thermal stabilization of irradiated polyethylene can also be accomplished [221, 254] with the help of the industrial antioxidants - aromatic amines and phenols, which are usually used in a concentration of 0.2% for the protection of polyolefins during technical processing, but introducing them in a considerably greater (10-20 times) quantity. These substances, introduced into polyolefins prior to irradiation in small (0.2-0.5 wt %) concentrations, exert an antirad influence on the polymer [247]. Protection is apparently of the "sponge" type. During the irradiation of a polymer in the presence of atmospheric oxygen (or traces of it during irradiation in a vacuum or a medium of inert gas) these compounds fulfill the functions of an antioxidant, diminishing cross-linking through oxygen bridges and simultaneously blocking weak bonds, as a result of which the consumption of the absorbed energy of radiation on the breaking of the main chain of the polymer is averted. With a content of 5 wt % of aromatic

phenols, for example 2.2'-methylene-*bis*-(4-methyl-6-*tert*-butyphenol), or amines, for example *di*-β-naphthyl-*n*-phenylenediamine, polyethylene which is irradiated up to the optimal dose retains a high elasticity (the relative elongation drops only by 25-30% as compared with original value instead of 70% in the absence of these additives; the content of gel fraction in this case is equal to 70% instead of 90% during irradiation without additives).

Phenyl-β-naphthylamine and ionol are also active antioxidants for irradiated polypropylene [223, 224].

The methods developed for thermal stabilization are also applicable to the irradiated copolymer of ethylene with propylene [255] - a material which presents special interest as an object for radiation modification for two reasons: 1) as a material possessing considerably higher deformation characteristics in the initial state and 2) as being cross-linked to the necessary degree in a lesser irradiation dose than polyethylene.

In a number of works [97, 256] for increasing the duration of the utilization of products made from irradiated polyethylene at elevated temperatures it is recommended to introduce as an additive prior to irradiation sulfur, selenium, tellurium, or compounds of them.

Until recently the inhibiting action of antioxidants were usually connected only with their purely chemical interaction with the polymer, but such an approach is not exhausting. In works [257, 258] the question was raised for the first time concerning the influence of heat stabilizers on structuration in the initial polymer and the change in the structure of irradiated polyethylene during thermal oxidation.

The comparison of the data of electron-microscopic and electron diffraction studies, differential thermal analysis, X-ray diffractiometry, and the strength characteristics of the polyethylene of low density both in the pure form and containing heat-stabilizing additives (separately and in various combinations) before and after irradiation, and also after thermal oxidation aging allowed the making of completely definite conclusions.

As the studies on model systems showed (films obtained from solutions in xylol), the individual components of heat-stabilizing systems, depending on their structure, properties, and also compatibility with the polymer, participate in the crystallization of polyethylene (Fig. 12a) as a nuclei forming agent (Fig. 12b) or plastifier (Fig. 12c). In a particular case both these functions can be fulfilled by one and the same component of the system. The introduction into a polymer of an optimal concentration of a heat-stabilizing system, the components of which are a nuclei forming agent and a plasticizer, predetermines the formation of the structure characterized by the interpenetration of the fibrils of adjacent spherulites and the disappearance of boundaries between individual spherulites, i.e., as a self-reinforcing of the system (Fig. 12d). Such a structure is observed for all the previously developed effective heat-stabilizing systems in their optimal concentration in a polymer.

The crystallization of polymer from a melt into a block in the presence of individual additives leads to the same results as in model systems - to cocrystallization in the case of an additive-nuclei forming agent and to the formation of large supramolecular structures in the case of an additive-plasticizer.

In Fig. 13a a picture of pure polyethylene is shown. The cocrystallization of polyethylene with a heat-stabilizing system in the optimal concentration leads to the formation of close-packed, perfect supramolecular structures (Fig. 13b), which correlates with the physicomechanical properties observed.

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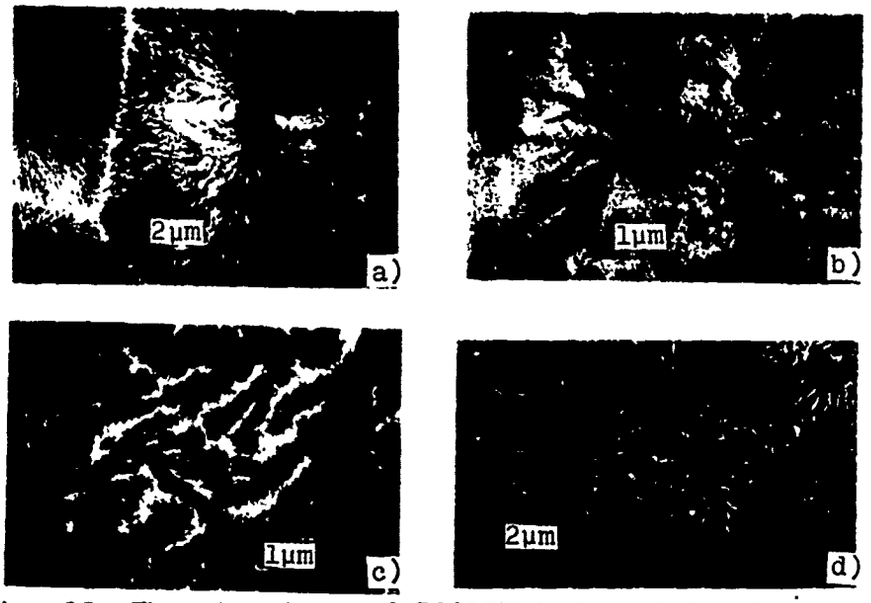


Fig. 12. The structure of P2015K industrial polyethylene of low density crystallized from a solution in xylol: a) pure polyethylene; b) polyethylene + 100 parts by weight of crystallizing additive; c) polyethylene + 20 parts by weight amorphous additive; d) polyethylene + + mixture of additives (crystallizing and amorphous) in an optimal concentration.

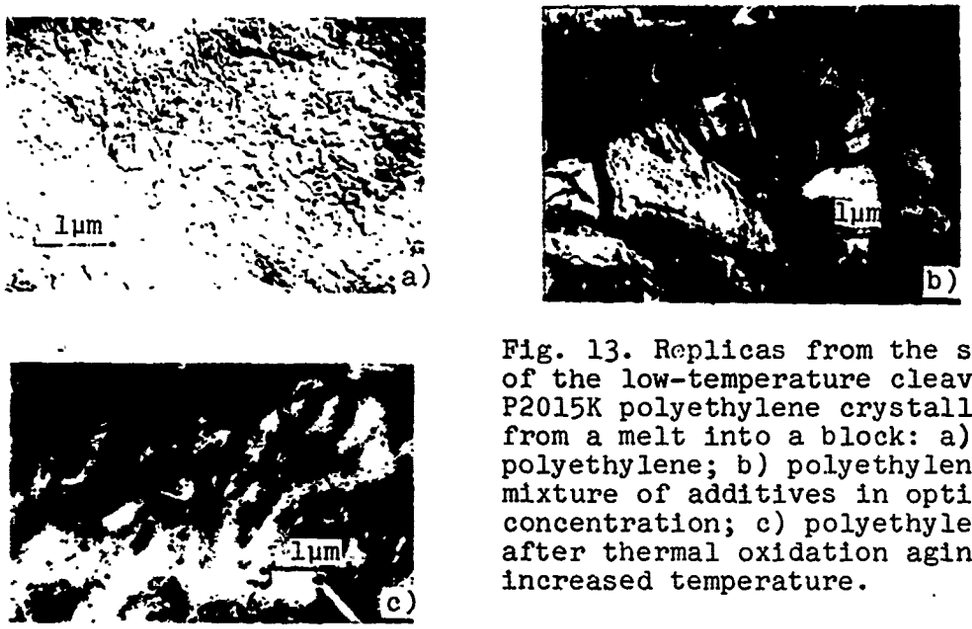


Fig. 13. Replicas from the surface of the low-temperature cleaving of P2015K polyethylene crystallized from a melt into a block: a) pure polyethylene; b) polyethylene + a mixture of additives in optimal concentration; c) polyethylene after thermal oxidation aging at increased temperature.

Thermal oxidation of irradiated pure and heat-stabilized polyethylene is accompanied by structural homogenization (Fig. 13c). Here the presence of heat-stabilizing systems predetermines the possibility of the subsequent recrystallization and thereby the preservation of physicomechanical properties for a prolonged period of aging. The data of X-ray defractometry show that pure polyethylene during thermal aging becomes amorphous rapidly, whereas in heat-stabilized polyethylene the degree of crystallinity is lowered only insignificantly.

Thus the totality of findings shows that the action of stabilizers upon their introduction into polyethylene is not limited to a purely chemical inhibiting effect. More perfect supramolecular structures which appear in the presence of heat stabilizing systems introduced in optimal concentrations and the nature of their mutual arrangement and packing (the interpenetration of fibrils which generate spherulites) hamper the process of oxidation. The presence of additive which is a nuclei forming agent predetermines the possibility of recrystallization during aging. The presence of a plasticizing additive increases the mobility of chains and individual structural elements, which also facilitates the processes of recrystallization after deep thermal oxidation degradation. Hence it follows that the phenomenon of synergism is conditioned for the most effective heat-stabilizing systems apparently not only by the purely chemical mechanisms examined earlier, but also to a considerable degree by the mechanism of unique "structural" protection, whereupon the determining factors which influence the thermal oxidation aging of irradiated polyethylene are the nature, perfection, and the packing density of the supramolecular structures of polyethylene.

This new approach to the problem of the thermal stabilization of polymers in general and irradiated polymers especially opens new possibilities for the "construction" of heat-stabilizing systems based on other principles, taking into account both the

inhibiting effectiveness of individual components and their influence on the processes of structuration.

The Sensitizers of Radiation Cross-Linking

It was shown above that all the polymer materials can be divided into two large groups - cross-linked and degradation polymers. Radiation treatment leads, as it will be shown below, to the improvement in the complex of properties only of cross-linked polymers, whereas for the achievement of efficiency it is necessary to irradiate the polymers up to very high doses. To degradation polymers the method of radiation cross-linked naturally is inapplicable. However, in recent years a method was proposed for the sensitization of the process of radiation cross-linking of polyolefins and some other polymers which makes it possible to substantially decrease the irradiation dose necessary for the modification of the cross-linked polymers, and also to carry out the radiation cross-linked of degradation polymers. This method consists of the following: into the polymer prior to irradiation some polyfunctional monomer is introduced as an additive [259-263].

Some authors have shown [262, 263] that the introduction of polyfunctional monomers (allyl acrylate, allyl methacrylate, and others), along with a significant decrease in the irradiation dose necessary for cross-linking, eliminates the undesirable side process of dehydrochlorination which flows during the irradiation of haloid-substituted polymers. Later it was established [264-266] that it was feasible to apply this method to the sensitization of the process of radiation cross-linking of a wide circle of polymers - polyvinyl acetate, polyethyl methacrylate, polypropylene, polyacetate cellulose, nylon. This method was also applied for the radiation solidification of unsaturated polyster resins [267].

In works [221, 268-272] a detailed investigation is made of the process of radiation cross-linking of polyethylene,

polypropylene, and polyisobutylene with additives of polyfunctional monomers: allyl acrylate, allyl methacrylate, divinylbenzene, ethylene glycol dimethacrylate, ethylene glycol diacrylate, triallyl phosphate, and others. The investigated monomers were introduced into the samples of polyethylene and other polymers by means of swelling to an equilibrium state at 25°C, then these systems were irradiated on a γ-source and the content of gel fraction determined by means of their extraction by xylol in the presence of antioxidants. By the introduction of the indicated additives (2-4 wt. %) it was possible to lower the dose of gel formation of 1 Mrad for pure polyethylene to 0.05 Mrad for the polymer - monomer system. The form stability of polyethylene at 130°C, irradiated after swelling in these monomers up to 1.2 Mrad, is no different from the form stability of pure polyethylene irradiated up to 30 Mrad. It was found [273] that the irradiation of pure polyethylene up to 80 Mrad gives rise to the same change in properties as during the irradiation of polyethylene in the presence of polyfunctional monomers in small doses. The dielectric properties of polyethylene are not very sensitive to the presence of these substances.

The effectiveness of radiation cross-linking of polypropylene, irradiated after swelling in polyfunctional monomers to equilibrium, also increases considerably. With an irradiation dose of 5 Mrad the content of gel fraction in the polymer - monomer system reaches ~70%, whereas in pure polypropylene in this dose a gel fraction is not formed at all. It is significant that for polypropylene this method of sensitization proves to be even more effective than for polyethylene, since the radiochemical yield of radicals during the irradiation of polypropylene is higher than for polyethylene. A very effective sensitizer of the process of radiation cross-linking of polypropylene is [221] triallyl cyanurate; it is also effective for polyethylene [274].

There is special interest in the use of the described method of sensitization of radiation cross-linking for polyisobutylene

wnich contains the quaternary atom of carbon, and because of this feature of chemical structure predominantly undergoes degradation during irradiation. As shown in work [275] by means of the analysis of the yield of gaseous products depending on dose and temperature during irradiation, degradation is mainly the result of the direct breaking of C–C bonds and not any other reactions leading to the liberation of gas. The analysis of infrared and untraviolet spectra [276] also confirmed this point of view. At the same time the introduction of some liquid additives, depending on additive concentration, can lead both to an increase and to a decrease in the number of breaks in the main chain [277]. By means of the appropriate selection of the polyfunctional monomer the trend of radiochemical processes which are developed in polyisobutylene during irradiation can be displaced to the side of cross-linking. At an irradiation dose of 1 Mrad pure polyisobutylene is completely degraded, whereas with the addition of allyl acrylate the content of gel fraction in this dose reaches 60% [270].

A study has been made of the influence of the nature of the mediums (air, vacuum) during the irradiation of the polymer - monomer system and the dependence of the reaction yield of radiation cross-linking on the irradiation dose [221, 255]. On the basis of the analysis of the infrared spectra of polyfunctional additive and irradiated compositions of polyethylene with these additives a mechanism is proposed for the sensitization of the reaction of radiation cross-linking. Specifically it has been established that the sensitizing action of polyfunctional monomers on the cross-linking of polyethylene is expressed at doses no higher than 40 Mrad.

In a subsequent work [271] the structural changes in the polymer - monomer system during irradiation are investigated and also the influence of the method of introduction of the polyfunctional monomer into the polymer on the behavior of the

resulting composition during irradiation and the reaction yield of radiation cross-linking are clarified. In this case it has been established that during irradiation not only does the addition of the polyfunctional monomer to polymer macroradial occur (useful effect), but also partially the polymerization of an additive itself (undesirable effect). It has also been shown that the effectiveness of the sensitizing action of the additive to a considerable degree depends on the method of its introduction into the polymer; heat treatment during introduction facilitates the polymerization of the additive itself, which substantially lowers its effectiveness during radiation cross-linking. It is necessary to take this into account when developing industrial technology. The results obtained agree well with the data of work [269].

In work [278] a method is proposed for the modification of a number of polymers (polyethylene, polyacrylonitrile, cellulose acetate, polyvinyl chloride, polymethyl methacrylate, and others) which leads to a decrease in their fluidity and solubility. A distinctive feature of this method lies in the fact that the polyfunctional monomers, which are the sensitizers of radiation cross-linking, are introduced into the polymer either by mechanical mixing or by means of swelling in a monomer, or finally by means of swelling in a mixture of monomer with an auxiliary liquid solvent in which the polymer being irradiated will swell sufficiently.

For the acceleration of the process of cross-linking of a number of polymers (linear polyamides, linear polyacetyls, halogenated and haloid-sulfonated 1-alkanes and vinyl polymers) it is suggested [279, 280] to conduct irradiation in the presence of 0.01-10% additive of tetrafluoroethylene, hexafluoropropylene, or perfluorocyclobutene. In this case along with an increase in the yield of cross-linking a product with a lower friction coefficient is obtained.

The effectiveness of the cross-linking of polyethylene and polypropylene can be also increased by means of their irradiation in the presence of monodichlorobenzene to the extent of more than 10% of the weight of the polymer. This method can also be used for polymers with fillers [281].

The acceleration of radiation cross-linking of styrene is attained in the presence of pyrene [282] and also triallyl isocyanurate [283].

In works [151, 173] a study is made of the influence of various gaseous media on the process of radiation cross-linking of polyethylene and it is shown that nitrous oxide exerts a noticeable sensitizing action. In subsequent works [175, 177] the influence of dose rate, temperature and pressure of the nitrous oxide on this process is investigated in detail.

In work [177] it is shown that during the irradiation of polyisobutylene in an atmosphere of nitrous oxide the yield of the process of degradation characteristic for this material diminishes as compared with irradiation in the air and in a vacuum.

In work [174] it is proposed that during the irradiation of polyethylene in an atmosphere of N_2O the process of cross-linking is sensitized and the probability of breaks in the main chain is not changed. At the same time for polypropylene irradiated in nitrous oxide a slowing down of the process of degradation has been uncovered [179, 221]. The opinion has been expressed [176] that the sensitizing action of nitrous oxide is apparently conditioned by the molecular excitation of N_2O and by their interaction with the hydrogen of the polymer chains, which gives rise to the liberation of molecular nitrogen and water, and also to cross-linking in the polymer.

The possibility of a lowering in the irradiation dose in the presence of a cross-linking agent - sulfur monochloride - is studied in work [284]; the processing of polyethylene films with a thickness of 60 μm and polypropylene threads with a thickness of 180 μm with sulfur monochloride was accomplished from the vapor phase, and then they were irradiated. It has been established that the cross-linking of polyolefins in the presence of sulfur monochloride occurs considerably more rapidly: 98% content of gel fraction is attained with a dose of 0.1 Mrad [285].

The mechanism for the sensitizing action of polyfunctional monomers on the process of the radiation cross-linking of polyolefins and other polymers can be presented in the following manner. The primary stage of the process is the clevage of the double bonds of the polyfunctional monomer under the influence of radiation. Further the molecule of polyfunctional monomer activated thusly interacts with the continguous polymer chains or macromolecules, which also gives rise to the formation of a cross bridge - a molecule of monomer imbedded between the polymer chains.

The indicated process is developed by a radical mechanism, which is confirmed [272, 286] by the absence of the dependence of yield of cross-linking in the polymer - monomer system on the dose rate and presence of inhibitors of radical polymerization.

Table 13 shows the content of gel fraction, %, in polyethylene depending on form and the sensitizing additive content at various irradiation doses in a vacuum.

The trend of work noted above on the lowering in the irradiation dose for the realization of the optimal complex of properties of radiation-modified polymers unconditionally has very important practical value, and although this method is still at the stage of industrial testing its investigation in various aspects embeds this possibility in the near future.

Table 13. The content of gel fraction in irradiated samples of polyethylene.

Sample	Concentration of additive, mole/kg	Irradiation dose, Mrad.			
		0.25	2	10	50
Polyethylene without additive	-	-	12	41	85
Polyethylene + allyl methacrylate	0.16	16	51	70	87
	0.25	21	32	60	86
	0.5	29	40	66	86
Polyethylene + triallyl cyanurate	0.25	45	71	87	91
	0.5	48	77	90	94
Polyethylene + ethylene gycol dimethacrylate	0.1	22	45	75	87
	0.25	25	47	75	89
	0.5	32	47	70	89
	1.0	37	55	83	90
Polyethylene + diallyl maleate	0.25	20	32	65	85
	0.5	22	45	83	87
	1.0	25	46	88	90

CHAPTER III

THE INFLUENCE OF IRRADIATION ON THE PROPERTIES OF ELECTRICAL INSULATING POLYMERIC MATERIALS

In the preceding sections it was shown that the influence of ionizing radiations, depending on the peculiarities of structure of the macromolecules of the initial material, the conditions of irradiation, temperature of the polymer, its phase state, presence of any additive, and other factors, lead to a significant change in the structure of the polymer: to transformation from linear (branched) into steric, to an increase or decrease in molecular weight, to the accumulation of some and the disappearance of other types of double bonds, etc. It is natural that all these changes have a significant influence on the various properties of a material and can lead both to the improvement (of some) and to the deterioration (of others) of its technical characteristics. Therefore the question of the influence of irradiation on the properties of electrical insulating materials is of significant interest at least in two directions.

In the first place, if the influence of ionizing radiations leads to an improvement of specific properties of the polymer, then, apparently it is possible to use irradiation as a technical method for the realization of a directed change in the properties of this material and thereby add to it the required characteristics.

In the second place, if under the influence of ionizing radiations some properties of the polymer deteriorate, then it is important to know under exactly what radiation conditions (taking into account the other factors it is understood) these properties deteriorate so much that the part no longer corresponds to its requirements, i.e., it loses the required technical characteristics; in other words, it is of interest to know the radiation stability of the material (evaluated by some criterion which is critical for the given application).

The complexity, and sometimes also the contradictoriness of requirements for materials and products during the creation of contemporary devices, machines and apparatuses, conditions the necessity for a complex approach when evaluating their efficiency for any operating conditions.

Taking into account the aforesaid below the changes in the properties of polymers of various classes under the influence of radiation are examined, and also the specifics of exploitation and the efficiency of electrical insulating polymeric materials in the zone of action of ionizing radiations as well as under conditions of space are noted.

THE CHANGE IN THE PROPERTIES OF POLYMERS UNDER THE INFLUENCE OF IONIZING RADIATIONS

Hydrocarbon Plastics

Polyethylene

Polyethylene is a hydrocarbon polymer with the structure $(-CH_2-CH_2-)_n$; it is obtained by polymerization of ethylene with the utilization of a heterogenic catalyst or very high pressures. The molecular weight of polyethylene varies usually within the

limits of 10^4-10^6. The main chain of the polymer consists of $-CH_2-CH_2-$ links but always there is also vinylidene, vinylene and vinyl nonsaturation, and also a certain branching whose degree depends on the method of obtaining. At room temperature polyethylene is partially crystalline and partially amorphous.

During irradiation in polyethylene processes of cross-linking and degradation flow, however, the first prevails over the second (the ratio of the rates of degradation and cross-linking comprises about 0.3). The formation of cross-linking has a significant influence on the properties of the material.

Thermomechanical characteristics (the deformation-temperature dependence). Figure 14 shows the thermomechanical curves of low [PNP] (ПНП) and high [PVP] (ПВП) density polyethylene irradiated by γ-radiation of Co^{60} under various conditions [287]. In both cases a difference is distinctly observed in the behavior of the nonirradiated and irradiated polyethylene. Equilibrium deformation during the action of a constant load at elevated temperatures is expressed less, the greater the irradiation dose and at any given dose is preserved practically constant up to the temperature of thermal decomposition of the polymer.

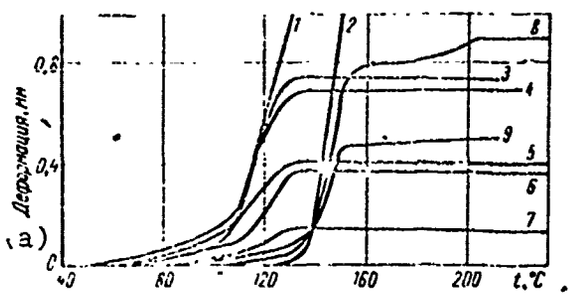


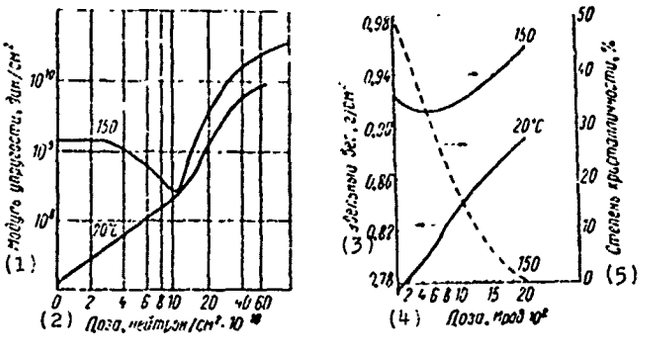
Fig. 14. The thermomechanical curves of polyethylene of low and high density, irradiated by γ-radiation in various doses: 1 - PNP (polyethylene of low density) nonirradiated; 2 - PVP (polyethylene of high density) nonirradiated; 3 - PNP, 50 Mrad; 4 - PNP, 65 Mrad; 5 - PNP, 100 Mrad; 6 - PNP, 155 Mrad; 7 - PNP, 240 Mrad; 8 - PVP, 50 Mrad; 9 - PVP, 100 Mrad
KEY: (a) Deformation, mm.

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The strength properties of polyethylene at a given temperature are directly connected with its crystallinity, the degree of which depends on molecular weight and the branching of the polymer. The crystalline phase of PNP at room temperature comprises 50-60%, but with a temperature increase its constant is lowered and it reaches zero at approximately 106-110°C, i.e., at the melting point of the greatest crystalline areas. In PVP content of crystalline phase at room temperature is higher (about 80%), but it also drops to zero at approximately 135-137°C, which coincides very closely with the theoretical melting point of infinitely long chains of n-paraffins. The comparison of properties of nonirradiated PVP and irradiated PNP shows that the difference between them is retained over a wide range of temperatures. Because of greater crystallinity PVP is softened at higher temperatures than PNP, but being heated to a temperature above 135°C it is converted into a viscous liquid and flow. After irradiation PNP acquires a reticular structure; at moderate dose of irradiation it also melts at temperatures of 110°C, however, even with a further temperature increase it does not flow, but it remains in a viscoelastic state and under the action of a certain load retains a final value of equilibrium deformation determined by the irradiation does (the denseness of the network). Thus,irradiation increases the thermostability of polyethylene in the sense that it ensures the form stability at temperatures which exceed the melting temperature of this polymer.

The modulus of elasticity. In Fig. 15a the dependence is shown of the modulus of elasticity of polyethylene on the irradiation dose in a reactor [288] at temperature of 20 and 150°C. The presence of a minimum in the curve taken at 20°C is explained by the course of two oppositely directed processes: the lowering in the degree of cyrstallinity under the action of ionizing radiations, leading to the decrease in modulus, and

the increase in the degree of structuration which raises the modulus, and we exclude the influence of crystallinity (heating to 150°C), then the modulus increases monotonically with an increase of irradiation dose.



a) b)

Fig. 15. The dependence of the modulus of elasticity a), specific gravity and the degree of crystallinity b) of polyethylene on the irradiation dose. KEY: (1) Modulus of elasticity, dyn/cm^2; (2) Dose, neutron cm$^2 \cdot 10^{18}$; (3) Specific gravity, g/cm^3; (4) Dose, Mrad$\cdot 10^2$; (5) Degree of crystallinity, %.

Density and degree of crystallinity. Symbatically with the modulus there is a change in polymer density during irradiation. Figure 15b shows the dependence of polyethylene density at 20 and 150°C, and also the degree of crystallinity on the dose of irradiation [289]: the deterioration of crystalline structure and degradation of chains diminishes density, whereas the formation of transverse bonds and a steric network increase it. Therefore the curve taken at 20°C has a minimum, and at 150°C increases monotonically.

For the deterioration of crystallinity in polyethylene of high and low density very large irradiation doses are required: $\sim 3.5 \times 10^9$ rad [290].

The doses given by various authors as being necessary for the complete deterioration of crystallinity in polyethylene differ quite strongly (compare [197, 290, 291]). This is apparently connected with differences in the properties of the initial material, and also by the differences in the conditions of

irradiation in different experiments (reactor, γ-source, electron accelerator). However, it has been noted [291] that for the complete destruction of crystallinity it is necessary to have substantially lower doses, if irradiation is conducted at temperatures which exceed the melting point of polyethylene.

This is connected with the fact that the cross-linkages which are formed during the irradiation of molten polymer fix in it a less ordered conformation of chains.

In the range of irradiation dose utilized in practice for the modification of properties (up to 100 Mrad) the degree of crystallinity of polyethylene is not substantially changed. However, the subsequent heating at temperatures above the melting point in an inert medium gives rise to the breaking up of crystallites into smaller units and therefore to a lowering in the temperature of melting (cross-linkages, being strained, during heating are able to relax) [252].

In work [292-294] it was shown that the melting point of polyethylene is lowered in proportion to the increase in the irradiation dose. At high irradiation doses the polymer as a result of this becomes transparent. An investigation of the change in the transparency of polyethylene Marlex-50 during irradiation showed [295] that the optimum conditions for obtaining a transparent polymer with good physical properties is irradiation up to a dose of 50 Mrad at a temperature higher than the melting point with subsequent irradiaiton up to a dose of 50 Mrad at room temperature.

Deformation characteristics. For the practical use of polyethylene in the active zone of ionizing radiations, and also for the selection of the optimal dose during modification it is important to know the dependence of its deformation properties

(tensile strength and relative elongation) on the irradiation dose. As the results of the investigations showed [287, 296], the nature of change in tensile strength and relative elongation with the irradiation dose depends significantly on the conditions of irradiation, and in certain cases - also on the ratio of the surface of the sample to its volume (Figs. 16 and 17).

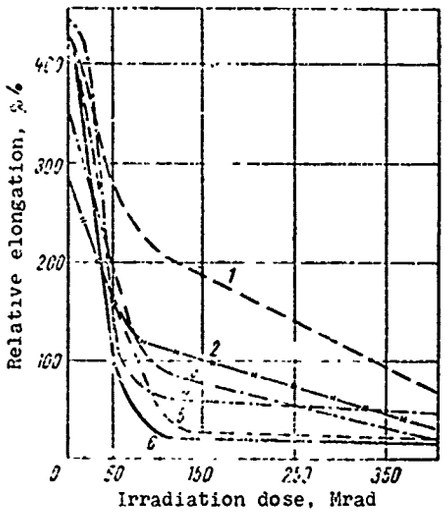
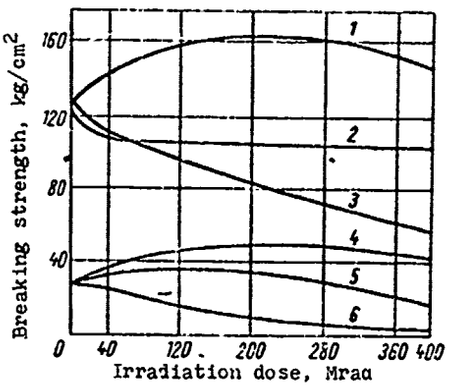


Fig. 16. The dependence of the relative elongation of samples of polyethylene on dose of γ-radiation:

	Irradiation dose, Mrad	Thickness, mm	Temperature of measuring, °C
1	Vacuum	0.4	20
2	The same	0.4	90
3	Air	0.95	90
4	"	0.95	20
5	"	0.4	90
6	"	0.4	20

Fig. 17. The dependence of breaking strength of samples of polyethylene on dose of γ-radiation:

	Conditions of irradiation	Thickness, mm	Temperature of measurement, °C
1	Vacuum	0.4	20
2	Air	0.95	20
3	"	0.4	90
4	Vacuum	0.4	90
5	Air	0.95	90
6	"	0.4	90



The influence of γ-radiation of Co^{60} in a vacuum leads to a strengthening of polyethylene at room temperature, however,

elongation decreases and in the range of doses of 100-200 Mrad it comprises ∿200%; analogously the characteristics are changed at an increased temperature - tensile strength increases and elongation is lowered to 100%. An increase in the irradiation dose of more than 200 Mrad conditions a certain lowering in strength and the further drop in relative elongation. Irradiation in air of samples with a thickness of 0.4 mm lowers both the relative elongation and tensile strength at both temperatures of testing. Samples with a thickness of 0.95 mm with respect to the change in strength characteristics as a result of irradiation in the air occupy an intermediate position between thin samples irradiated in the air and in a vacuum. Such a dependence of change in properties on the presence of air and thickness of sample attests, on the one hand, to the large role of oxygen in processes of radiolysis of polyethylene [297], and on the other - to the limiting influence of diffusion of oxygen into polyethylene on the radiation oxidation of the latter at the dose rate used (10^2-10^3 rad/s).

As shown in work [296] the tensile strength of polyethylene of low density begins to increase in the range of doses of 5-10 Mrad and increases with further irradiation up to doses of 150-200 Mrad, whereupon it begins to diminish. According to work [78] the decrease in tensile strength begins after irradiation up to doses of 100 Mrad.

An increase in tensile strength already in the area of small doses is apparently conditioned by an increase in the average molecular weight.

Tensile strength of high-density polyethylene also increases with an increase in irradiation dose, and even to a greater extent than in low-density polyethylene.

The relative elongation of low-density polyethylene in the area of small doses increases a little and then in proportion to the increase of dose decreases.

An increase in relative elongation at low doses can be connected with the plasticizing action of the low molecular fraction which is formed during irradiation, and also as a result of the certain increase in molecular weight.

With an increase of irradiation dose in the polymeric matrix increasingly more cross bonds are formed, as a result of which the cold flow of the polymer is impeded increasingly more. The decrease observed in relative elongation with an increase of dose is conditioned by the replacement of relatively weak van der Waals' interaction forces on the primary valence bonds between the polymer chains. With an increase in the density of the steric network the possibility of the mutual displacement of chains diminishes and elongation drops off. The decrease of relative elongation with an increase of dose is one of the fundamental limiting factors which determine the possibility of the utilization of polyolefins in radiation fields and the industrial use of radiation cross-linked polymers.

The description of the influence of orientation on the properties of cross-linked system is given in the works [298 to 300].

Resistance to tear. Investigation of resistance to tear of low-density polyethylene by the ASTM-1004 method [292] showed that irradiation over the range of doses of 0-64 Mrad practically does not change this characteristic.

Creep. The irradiation of polyethylene leads to noticeable changes in creep (deformation at a constant load) of this polymer.

In Table 14 data are given form works [148, 301] on the measurement of creep of low-density polyethylene irradiated by γ-quanta at 25°C. During testing samples in the form of the disk with a diameter of 25.4 mm and load of 60 kgf were used. From the table it is clear that during the irradiation of polyethylene even up to very low irradiation doses creep under the action of applied stress is lowered, and elastic recovery increases.

Table 14. Creep and the elastic recovery of irradiated polyethylene of low density.

Dose of irradiation, Mrad	Maximum creep at 30°C; resilience, cm $cm^2/dyne \times 10^9$		Deformation of linear dimensions after compression at 132°C, % of initial thickness		Elastic recovery after testing for creep at 30°C for 10^4 s, %	
	10 s	10^4 s	11 min	15 min	after 10 s	after 10^4 s
0	1,56	2,33	0,22	0,12	50,4	69,5
1	1,42	1,80	0,30	0,16	78,6	100
5	1,15	1,57	0,47	0 37	73,5	79,5
10	0,93	1,15	0,50	0,41	71,5	100
20	1,09	1,20	0,65	0,61	76,5	100
40	0,81	1,06	0,78	0,69	85,5	100
64	0,80	0,80*	0,84	0,84	—	—

*Sample defective.

It is doubtless that the increase in stability of creep is conditioned by the cross-linking of polymer chains.

Creep of the nonirradiated and irradiated high-density polyethylene was investigated at temperatures of 20-90°C and it was revealed that the characteristics of creep depend on the dose and the medium in which irradiation was conducted [302]. Samples irradiated in a vacuum are more stable to creep, the deformation of the latter diminishes with an increase in the degree of cross-linking by the following law:

$$\varepsilon_t = \varepsilon_0 e^{-\alpha s},$$

where ε_r - the deformation of creep of the irradiated sample; ε_0 - the deformation of creep of the nonirradiated sample; x - the degree of crystallinity; a - the constant dependent on temperature and applied stress.

Irradiation in air barely changes the stability to creep, which is connected with the course of radiation-oxidative degradation.

Resistance to cracking under stress conditions. It is known that the resitance of polyethylene to cracking under stress conditions depends on the peculiarities of the medium and the temperature. It was shown that the degree of the ambient effect is defined mainly by the molecular weight of the polymer while the degree of the temperature effect - by its crystallinity. The irradiation of any polyethylene leads to an increase in resistance to cracking under stress conditions (Table 15).

Table 15. The resistance of high-density polyethylene to cracking under stress conditions.

Material	Irradiation dose, Mrad	Time after which 50% of samples do not pass, h the tests
Alathon-10	0	0.3
	0.5	0.3
	2	1.3
	8	>3.0 months
DYNH	0	0.3
	0.5	0.3
	2	26
	8	504
	32	>3.0 months
	64	The same
DYNH with antioxidant (dinapthyl-n-phyenylenediamine	0	0.3
	0.5	0.3
	2	4.5
	8	504
	32	>3.0 months
	64	The same

It is evident from Table 15 that low-density polyethylene of various brands after irradiation up to doses of 8 Mrac and higher does not crack. The resistance of high-density polyethylene to cracking also can be increased with the help of irradiation; the irradition dose necessary for this depends on molecular weight and the degree of crystallinity of the polymer. For the majority of industrial brands of polyethylene an irradiation dose of 4-6 Mrad is required. The increase in resistance to cracking under stress conditions as a result of irradiation is connected with the increase in the average molecular weight as a result of the cross-linking of polymer chains.

Dynamic physicomechanical properites. The dynamic physicomechanical properties of polymer, measured with the application of sinusoidally changing stress, depend on molecular weight, the degree of branching, content of cyrstalline phase, density of cross-linkages, and orientation of the molecules.

This method is used in experiments with irradiated polyethylene. In work [304] there is a report on the temperature effect on the dynamic modulus of samples of polyethylene irradiated in a reactor up to various doses. With low temperatures the modulus diminishes with an increase in the irradiation dose until 2-6% of cross-linkages are formed, and then it begins to increase. These data are confirmed in work [303]. With a cross-linakge content up to 10% only insignificant changes are observed [309] in dynamic modulus, but with a further increase in the content of cross-linkages it begins to increase. Differences in the results of works [303] and [309] are connected with the fact that temperature during the irradiation was different: 75 and 40°C respectively.

The increase in dynamic modulus with the increase in irradiation dose is conditioned by the cross-linking of the

polymer. Although the degree of crystallinity diminishes with an increase in the irradiation dose, and this has to be expressed on the value of the modulus, the formation of primary valence bond facilitates an increase in modulus and compensates for the decrease in the degree of crystallinity. In later works the influence of irradiation on extinction in polyethylene of low [306] and high [307, 308] density was studied. It is noticed that the dynamic physicomechanical properties of polyethylene in the range of small doses practically do not change.

Solubility and swelling. Polyolefins, including polyethylene, are soluble in various hot organic solvents (aromatic hydrocarbons, chlorinated aromatic hydrocarbons, etc.). As a result of irradiation their solubility is lowered. After irradiation up to doses which exceed the gel point the polymer is completely insoluble. The three-dimensional network formed as a result of irradiation prevents the dissolution of polymer, and it can only be limited by swell, whereupon to a lesser degree, the higher the irradiation dose and therefore the density of cross-linkages. As can be seen from Fig. 18, with an increase in the irradiation dose swelling diminishes. This dependence as noted above, can be used for determination of the degree of cross-linking in polymers.

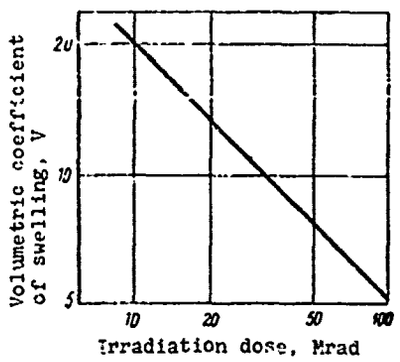


Fig. 18. The dependence of the volumetric coefficient of swelling of polyethylene on irradiation dose.

In work [311] the swelling of irradiated polyethylene is studied in the vapors of organic solvents depending on dose and the conditions of irradiation, and also on temperature. In this case basically the same regularity is valid as during swelling in a liquid.

Thermal conductivity. The temperature dependence of thermal conductivity was investigated for irradiated polyethylene over the range of temperatures of 0-170°C at doses up to 3100 Mrad, and a nonmonotonic course of this dependence was revealed [310]. The limiting value of thermal conductivity at temperatures above 100°C for low-density polyethylene is equal to $5.5 \cdot 10^{-4}$ cal/(cm·s·deg), and for high-density polyethylene - $5.8 \cdot 10^{-4}$ cal/(cm·s·deg). The nature of change in the coefficient of thermal conductivity depending on the irradiation dose is different for different temperature ranges. At 20°C thermal conductivity is lowered monotonically with an increase of dose, at 150°C with an increase in dose thermal conductivity is increased, reaching a certain limit.

The influence was investigated of neutron and γ-irradiation at 20°C on the coefficient of thermal conductivity of polyethylene of high and low density, caprone, polymethyl methacrylate, polystyrene, and some styrene copolymers [312, 313]. It has been shown that the coefficient of thermal conductivity for polyethylene, caprone, and polymethyl methacrylate decreases, but for polystyrene and its copolymers it increases. The thermal conductivity and other thermophysical parameters of irradiated polyethylene depending on temperature were also investigated [314]. The authors used the method of routine thermal mode. The values obtained for the coefficients of thermal conductivity λ, thermal diffusivity α, and specific thermal resistance ρ for cylindrical samples of polyethylene with a radial thickness of 2.3 mm are given in Table 16.

Thermostability. In work [244] the method of thermogravimetric analysis was used to investigate the influence of irradiation in air and in a vacuum at room temperature on the thermal and oxidative degradation of polyethylene (Marlex-50, molecular weight 520,000). It has been revealed that irradiated linear

polyethylene, independent of the conditions of irradiation, possesses less thermostability than nonirradiated and behaves approximately the same as strongly branched low-density polyethylene.

Table 16. The change of thermophysical parameters of irradiated and nonirradiated low-density polyethylene depending on temperature.

Polyethylene	Temperature, °C	λ, 10^{-4} W/(deg·cm)	a, 10^{-3} cm^2/s	ρ, 10^{-3} $\Omega_T \cdot cm$
Nonirradiated	115	6,15	3,07	15,2
	120	6,72	3,35	14,8
	125	6,81	3,41	14,6
Irradiated in a dose of 120 Mrad in argon (γ-radiation)	125	3,29	1,61	30,2
	150	4,74	2,36	21,0
	200	8,73	4,35	11,5
	250	45,10	22,50	2,2

A thorough analysis of the curves of differential thermogravimetric analysis showed that polyethylene irradiated both in a vacuum and in air is more subject to oxidative degradation than nonirradiated. However the losses of weight as a result of oxidative degradation of polethylene irradiated in a vacuum, are greater than that irradiated in air. This can be attributed to difference in the content of tertiary atoms of carbon.

With an increase in the dose of irradiation the thermostability of polethylene deteriorates.

Rheological characteristics. The melt index. In polyolefins which are predominatly cross-linked during irradiation with an increase in irradiation dose the molecular weight increases and this is manifested in an increase in the viscosity of fusion (the melt index). In Table 17 the change in the melt index is given [292] which was measured for various types of low-density polethylene depending on the absorbed dose. An analogous

regularity is also valid for high-density polethylene [315, 316] (Table 18). The rate of shear increases with an increase in shearing force.

Table 17. The dependence of the melt index of low-density polyethylene on the irradiation dose [292].

Dose of irradiation Mrad	Melt index*, g/10 min			
	DYNH		with antioxi-dant	Alathon-10
	190°C	267°C	190°C	190°C
0	1,16	9,77	2,10	2,25
0,5	1,02	5,93	1,50	1,56
2	0.3	1.14	0,30	0,25
32	Does not flow	Does not flow	--	--

*The melt index was determined according to ASTM D-1238

Table 18. The dependence of the melt index irradiation dose at 190°C for linear polyethylene [315].

Irradiation dose, Mrad	Melt index*, g/10 min		Irradiation dose, Mrad	Melt index*, g/10 min	
	Grex	Forti-flex		Grex	Forti-flex
0	4,20	5,22	1,32	1,88	2,01
0,22	3,92	4,55	1,76	1,21	1,43
0,44	3.29	3,77	2,20	1,00	0,82
0,66	2,80	3,22	3,03	0,35	0,13
0,88	2,39	2,92			

*The melt index determined according to ASTM D-1238

In work [222] an investigation is made of the influence of small irradiation doses (up to 1 Mrad) on the rheological properties of linear polyethylene and a copolymer of ethylene with propylene. It turned out that irradiation has little influence on thermal stability, tensile strength, flow limit, etc.

The authors proposed to use polyethylene irradiated up to small doses for conversion into products, because such irradiation still does not influence the viscosity of the melt at high shear rates (i.e., under conditions of conversion), but it facilitates an increase in the stability of form of the extruded products.

Table 19 contains reference data on the influence of radiation on the physicomechanical properties of polyethylene at high density and a copolymer of ethylene with propylene.

From the information given it is evident that irradiation up to small doses substantially changes the rheological characteristics of polyethylene while heat resistance and strength are not noticeably changed. The lowering in elongation during breaking already is completely perceptible, and flexibility and impact strength improve somewhat.

Analogous investigations, but already in a significant range of doses (up to 75 Mrad), have been carried out in work [317]. The composite results obtained for high-density polyethylene are given in Table 20.

The analysis of the data shows that the change in the viscosity of the melt during irradiation is greater, the less the original value of the melt index (and the greater the molecular weight). The softening temperature (according to Vicat) during irradiation up to a dose of 75 Mrad increases on the average by 10°C, whereas this characteristic does not really reflect the changes in the properties of the material (see thermomechanical characteristics), since at temperatues exceeding the melting point irradiated polyethylene does not flow, and its properties call more to mind pliable rubber than molten polyethylene [318]. Resistance to tension cracking under the action of surface-active compounds increases strongly after irradiation to a dose of a total of 5-10 Mrad.

Table 19. The influence of radiation on the physicomechanical properties of high-density polyethylene and a copolymer of ethylene with propylene.

Polymer	Irradiation dose, Mrad	Melt index, g/10 min	Softening temperature in Vicat test, °C	Density, g/cm³	Yield point, kgf/cm²	Tear resistance, kgf/cm²	Relative elongation, %	Number of bends up to failure	Impact strength according to Izod, kgf·s/cm
Polyethylene, d = = 0.959 g/cm³ with antioxidant (Santanox, 0.01 parts by weight)	0.0	1,87	127	0,959	316	248	950	800	15,7
	0.2	1,70	129	0,960	313	273	950	850	12,2
	0.4	1,47	130	0,960	323	244	630	850	15,7
	1.0	1,03	129	0,61	335	198	280	1100	19,7
Polyethylene, d = = 0,957 g/cm³ with antioxidant (Santanox, 0.02 parts by weight)	0.0	0,69	131	0,957	314	362	870	1750	37,3
	0.2	0,52	133	0,957	314	362	860	1850	31,8
	0.4	0,38	133	0,958	314	336	830	1600	37,8
	1.0	0,077	136	0,960	352	206	540	1050	39,5
Copolymer of ethylene with propylene, d = = 0.951 g/cm³ with antioxidant, 0.01 parts by weight	0.0	1,30	126	0,951	266	383	1100	900	19,8
	0.2	1,50	126	0,950	271	281	950	900	15,7
	0.4	1,15	126	0,950	266	331	1000	900	14,6
	1.0	0,48	126	0,951	270	288	920	900	18,1
Copolymer of ethylene with propylene, d = = 0,949 g/cm³ with antioxidant, 0.01 parts by weight	0.0	0,40	131	0,949	261	425	920	2600	38,4
	0,2	0,25	128	0,948	261	412	820	2500	37 3
	0,4	0,156	128	0,949	268	443	820	2500	39,6
	1.0	0,012	129	0,949	286	236	400	2450	37,4

Table 20. The change in rheological and physicomechanical characteristics of high-density polyethylene during irradiation up to small doses.

Sample	Irradiation dose, Mrad	Melt index, g/10 min (load 10 kg)	Density at 23°C, g/cm³	Softening temperature in the Vicat test, °C	Yield point, kgf/cm²	Tear resistance, kgf/cm²	Relative elongation, %	Impact viscosity, kgf/s	Number of bends up to rupture	Resistance to tension cracking (in Igepol)* hr
I	0	0,25	0,9407	113	243	315	740	63,8		267
	2	0,010	0,9467	117	245	342	750	59,5		492
	5	0,001	0,9476	112,5	257	310	740	53,4		378
	10	0,001	0,9476	116,5	245	314	680	76,5		>2000
	25	0,001	0,9476	118	258	246	330	125		>2000
	50	0,001	0,9474	118,5	255	300	200	103		—
	75	0,001	0,9484	120	257	318	170	91		—
II	0	2,6	0,9478	109	260	153	300	18,1	2240	22
	2	0,29	0,9478	108	264	157	550	17	744	57
	5	0,25	0,9484	108	260	155	560	18,1	705	495
	10	0,001	0,9484	112	262	155	530	21,4	(1090)	>2000
	25	0,001	0,9478	114	264	208	230	123	462	>2000
	50	0,001	0,9462	115	264	320	230	101	19	—
	75	0,001	0,9487	119	273	306	200	98	22	—
III	0	35,0	0,9497	102	266	140	180	71,5		0
	2	6,7	0,9497	102,5	256	140	140	7,7		—
	5	0,31	0,9501	105	264	144	130	7,7		22
	10	0,001	0,9501	106	255	154	130	8,8		334
	25	0,001	0,9493	111	264	184	230	33		>2000
	50	0,001	0,9489	115	263	234	170	114		—
	75	0,001	0,9489	114	269	283	270	108		—

*[Translator's note: Igepol is transliterated from the Russian].

Friction properties of polymers. In [319] a study is made of the dependence on dose of the friction coefficient μ and the value s/p, where s - resistance to shear, p - the fluidity of linear polymers irradiated by Co^{60} γ-radiation and it has been established that with an increase in the absorbed dose for the polymers being cross-linked, for example polyamid and high-density polyethylene, μ increases by two and four times respectively while for low-density polyethylene μ diminishes by two times as compared with the initial; for degrading fluorine-containing hydrocarbons the increase of μ is less than for cross-linked.

In another work [198] an investigation is made of the influence of various factors on the coefficient of friction and the wear of some irradiated polymeric materials (measurements were conducted at different temperatures) and it was revealed that with an increase in irradiation dose (up to $2.5 \cdot 10^9$ rads) and an increase in the degree of cross-linking wear is increased, whereupon the coefficient of wear is proportional to the irradiation dose if the dose exceeds a certain critical value. Apparently the degree of wear is connected with an increase in the brittleness of irradiated polymers and is determined by the surface temperature of the polymer during friction.

Diffusion characteristics. Permeability. Structural-chemical changes in polymer systems caused by the effect of radiation give rise to a change in water vapor and gas permeability of the polymer. During the investigations [320-322] it was revealed that there was a lowering in the permeability factor P and the activation energy of permeability E of polyethylene for various gases, vapors, and organic liquids at doses on the order of 20-100 Mrad.

An increase in the solubility of He, N_2, CH_4, and C_3H_8 in low-density polyethylene during irradiation in air has been revealed in work [323].

An investigation was made of the influence of ionizing radiations on the moisture permeability of polyethylene irradiated in air over the range of doses of 50-300 Mrad [324, 325]. It was established that with a change in the irradiation dose by 6 times the diffusion coefficient is reduced by three times, the permeability factor increases by almost 10, and the solubility coefficient - by 25 times.

The presence of a correlation between the increase in the coefficient of permeability and the value tg δ of the samples of polyethylene irradiated in air (taking into account the known mechanism of radiochemical processes which flow in this polymer during irradiation) made it possible to explain the result obtained by an increase in the content of polar groups in the material and respectively by the increase in the solubility of moisture in the sample. Direct experiments on the irradiation of polyethylene in a vacuum confirmed these assumptions [236].

The change in the permeability of polyethylene as a result of irradiation for the vapors of organic liquids, especially benzene, is described in works [311, 327].

Freeze resistance. The influence of irradiation on the elasticity of polyethylene at low temperatures has not been studied in detail. In works [292, 296] it was reported that the freeze resistance of low-density polyethylene is practically unchanged during irradiation. Since this value depends on molecular weight, in the case of small irradiation doses of 10-100 Mrad this property can even be somewhat improved. These data have been confirmed in work [251]. However, as shown in work [328], at doses greater than 1000 Mrad, when crystallinity is already disrupted, the low-temperature properties of polyethylene deteriorate and the polymer becomes brittle even at room temperature.

Atmospheric aging. During irradiation the structure of polyethylene is changed: in the molecules of polymer non-saturation emerges and polar groups are formed, for example carbonyl, hydroxylic, etc. It would seem that irradiated polyethylene should be less weather resistant than nonirradiated. However, it has been established that the weather resistance of polyethylene after irradiation even improves somewhat especially with the introduction of a small addition of soot. The samples of polyethylene irradiated up to comparatively small doses, and which contained finely dispersed soot, possess better weather resistance than nonirradiated. Following irradiation up to significant doses weather resistance deteriorates. Thus an increase in molecular weight, which is the result of radiation cross-linking, covers the certain ill effect conditioned by the accumulation of nonsaturation and of polar groups in the material

Thermal aging. In the preceding sections it was noted that irradiated polyethylene possesses form stability at temperatures exceeding the melting point and therefore the upper limit of the temperature range of its efficiency is the temperature of thermal decomposition. However, as it was already said, in air at elevated temperature irradiated polyethylene is oxidized, processes of degradation and structuration occur, and these changes in the structure of the material find reflection in changes in its properties, primarily in the physicomechanical characteristics. The most important, and sensitive to aging, characteristic of polyethylene is its elasticity, which can be evaluated according to the magnitude of relative elongation.

The study of this characteristic of irradiated polyethylene during aging for the evaluation of the possibilities of its practical utilization, for example as electrical insulation

(including cable products), has been treated in the works of both Soviet and foreign authors [296, 329-332]. The results obtained showed that polyethylene containing up to 0.2% of standard stabilizer (for protection of the polymer from oxidation during technical processing, but not during prolonged exploitation at increased temperature), irradiated up to the optimal dose, preserves its efficiency in air at 200-250°C for several hours, at 150°C - several dozen hours, and at 110°C - several hundred hours. The duration of operation at the indicated temperatures is limited by a sharp reduction in elasticity and by an increase in the brittleness of the material, which is connected with processes of oxidation which flow very rapidly at elevated temperatures. At the same time the prolonged storage of irradiated polyethylene at sufficiently high temperatures (250-300°C) in an oxygen-free atmosphere does not deteriorate its operating characteristics.

Therefore it is possible to increase the permissible duration of exploitation of irradiated polyethylene in the presence of air at increased temperatures in two ways: either by external (the utilization of protective sheaths, exploitation in a neutral atmosphere) or internal (the utilization of stabilizers which inhibit the oxidation process) protection. The first path is apparently sufficiently effective, but has been used far from in all cases.[1] The second path, while on the whole less effective, has a more universal application.

In this connection the authors developed [249] methods for the thermal stabilization of irradiated polyethylene which made

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[1]As the external protection of irradiated polyethylene at increased temperatures (150-175°C) they sometimes use a covering made from synthetic resins, especially polyester and phenol-formaldehyde. The resins are applied on the surface of the product from solution, whereupon after removal of solvent on the surface of the product there remains a fine film with a thickness of 0.012-0.25 mm which possesses high adhesion to irradiated polyethylene [334].

it possible to realize the potential possiblities of this material during exploitation.

In works [247, 253, 333] a study was made of the stabilization effect of a wide circle of chemical compounds and combinations of them in different proportions and on the basis of an analysis of changes in thermomechanical characteristics and strength properties of irradiated compositions of polyethylene with different additives it was established that it is possible to substantially increase the duration of use of irradiated polyethylene at increased temperatures.

Figure 19 shows the dependence of relative elongation of irradiated (100 Mrad, in helium) samples of polyethylene with a standard stabilizer (control) and compositions of it with single and combined additives on the time of stay in air at increased temperatures.

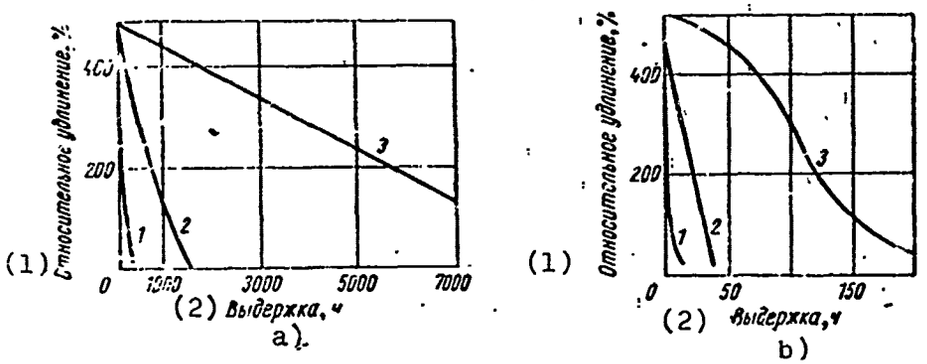
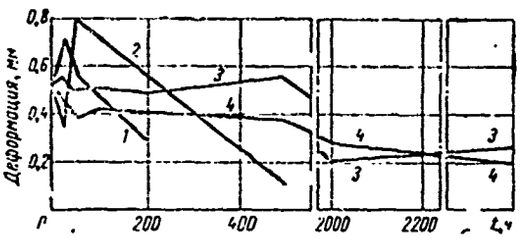


Fig. 19. The dependence of relative elongation of irradiated samples of cable polyethylene and compositions of it with single and combined additives on the time of stay in air at 150°C a) and 200°C b): 1 - cable polyethylene; 2 - composition with single additive, 10 parts by weight; 3 - composition with combined additive, 5 parts by weight.
KEY: (1) Relative elongation, %; (2) Holding time, h.

If as the criterion of the loss of elasticity we accept the lowering in relative elongation during thermal aging in air up to 100%, then the efficiency of irradiated polyethylene with a standard stabilizer comprises about 150 hours at 150°C and at 200°C - several hours. The addition to polyethylene prior to irradiation of single stabilizing additives increases its efficiency at 150°C up to 1000-1500 hours, and at 200°C - up to 30-40 hours. The utilization of the most effective combined additives increases the efficiency of polyethylene in air at 150°C to 7000-10,000 hours and at 200°C - to 150-200 hours.

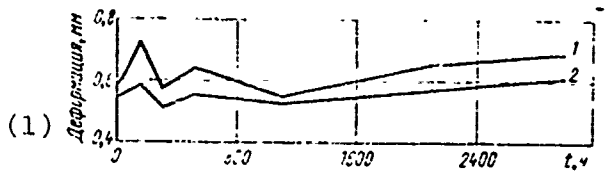
It is natural that the possibility of prolonged exploitation of irradiated polyethylene in the air at increased temperatures considerably expands the prospects of utilization of this material.

Figures 20 and 21 show the change in the value of equilibrium deformation of irradiated polyethylene during thermomechanical tests during prolonged aging in air and in an atmosphere of nitrogen correspondingly.



(1)

Fig. 20. The dependence of the value of equilibrium deformation of samples of polyethylene irradiated in nitrogen (100 Mrad) during thermomechanical testing under a load of 1 kgf on the duration of stay in the air at 150°C: 1 - cable polyethylene; 2 - composition of cable polyethylene with single additive, 10 parts by weight; 3, 4 - compositions of cable polyethylene with combined additives, 5 parts by weight.
KEY: (1) Deformation, mm.
Designation: ч = hour.



(1)

Fig. 21. The dependence of the value of equlibrium deformation during thermomechanical testing under a load of 0.5 kgf of the samples of cables with irradiated polyethylene 1 - and alkatene* 2 - insulation with a radial thickness of 0.4-0.5 mm on the time of stay in an atmosphere of nitrogen at 250°C.
KEY: (1) Deformation, mm.
Designation: ч = hour.
*[Translator's note: transliterated from cyrillic].

A comparison of the curves in Figs. 20 and 21 shows that the use of an effective combined system of heat stabilizers seemingly placed irradiated polyethylene which was subjected to thermal aging in the air in conditions close to aging in an atmosphere of a neutral gas.

Electrophysical characteristics.[1] Since polyethylene is used very widely as an electrical insulating material, for example for wires and cables, there is significant interest in the dependence of its dielectric properties on conditions and dose of irradiation.

Investigations in this field are covered in a significant quantity of works of both foreign and Soviet scientists.

Thus in work [335] the interesting relationship which joins the mechanical and electrical strength (under direct voltage) of polyethylene was established. The electrical strength of nonirradiated polyethylene decreases monotonically with an

[1]Here the irreversible changes observed after irradiation are mainly examined. The reversible effects and their influence are described in Section 2 of this chapter.

increase in temperature up to the melting point. The curve of dependence of electrical strength of irradiated polyethylene calls to mind the form of the curve of dependence of the modulus of elasticity on temperature. Moreover it is characteristic that the value of electrical strength diminishes in proportion to the temperature increase until all the crystallites are fused, and then it remains approximately constant. For the explanation of the resulting regularity an assumption was made that polyethylene breaks down as a result of mechanical reasons, and the electric field causes only the compression of polyethylene to a certain extent dependent on the modulus of elasticity.

The results of the study of the temprature dependence of specific resistance and the disruptive strength of polyethylene irradiated over the range of doses of 50-400 Mrad at temperatures from room to 400°C [336] are given in Figs. 22 and 23. Dependence lg R = f(t) is adaquately approximated by a straight line, whereupon at 300°C specific resistance comprises $\sim 5 \cdot 10^8$ Ω·m. The electrical strength of nonirradiated polyethylene is sharply lowered with an increase of temperature. The irradiation of polyethylene insulation substantially changes the nature of the temperature dependence of disruptive strength: it becomes considerably ess sharp, whereupon decay is less, the higher the irradiation dose. The absolute values of disruptive strength even at 300 to 400°C are sufficiently great.

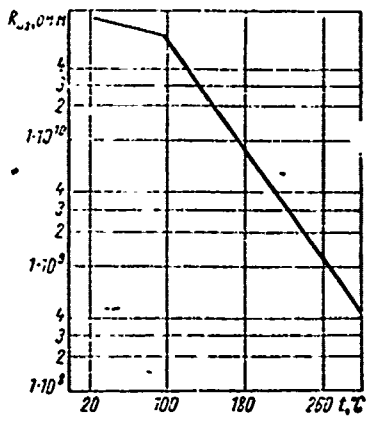


Fig. 22. The dependence of the specific resistance of irradiated polyethylene insulation on temperature. Designation: ом·м = Ω·m.

The dependence of the dielectric characteristics of polyethylene both during and after irradiation by γ-radiation and accelerated electrons over a

wide range of frequencies and temperatures is described in works [332-342].

In a previous stage a study was made of the influence of the braking radiation of a betatron with an energy of 15 MeV after irradiation up to 10^5 rad (dose rate of 500 rad/min) on the dielectric properties of polyethylene. It was established that ε, tg δ, ρ_v over a wide range of frequencies at temperatures of -70 to +70°C, and also under conditions simulating tropical (temperature of +40°C, relative humidity 98%), are practically unchanged (Fig. 24). The insignificant difference in the value of tg δ in the range of low frequencies during irradiation under "tropical" conditions is apparently connected with the interaction between the products of the radiolysis of water and the free radicals formed during the irradiation of polymers. Reversible effects in these experiments could not be revealed because the measurements were made 1-3 hours after the stopping irradiation.

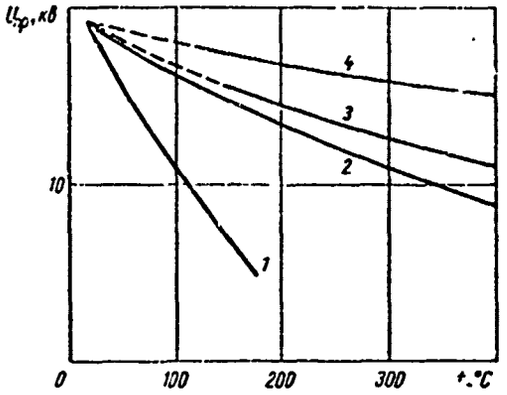


Fig. 23. The dependence of the disruptive strength of polyethylene insulation (thickness 0.4-0.5 mm) on temperature and irradiation dose: 1 - non-irradiated; 2 - 46 Mrad; 3 - 200 Mrad; 4 - 400 Mrad. Designation: кВ = kV.

A study of the same characteristics directly in the radiation field (at a dose rate of 670 rad/min) showed that tg δ at the moment of irradiation increases quite sharply, but practically does not depend on the absorbed dose and is instantly restored to the original values after the termination of irradiation. The degree of influence of γ-radiation on the change of tg δ substantially depends on the temperature conditions during the

irradiation; the increase of tg δ is greater, the lower the temperature of the sample during irradiation:

Temperature, °C	-70	+20	+40	+70
Increase of tg δ, % (as 100% the value of tg δ prior to irradiation is accepted)	240	41.5	16	6-7

The dependence of tg δ on the dose rate is subordinated to the law

$$\operatorname{tg}\delta \backsim \operatorname{tg}\delta_0 \cdot I^{\alpha},$$

where tg δ - the value measured in the irradiation field; tg δ_0 - the value measured prior to irradiation; I - the dose rate of irradiation; α - coefficient equal to 0.05-0.02.

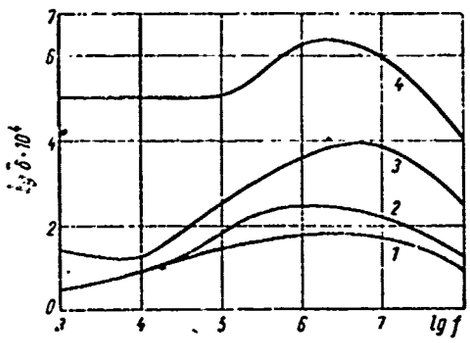


Fig. 24. The dependence of tg δ of unstabilized polyethylene on frequency at various doses of electron irradiation in air (limited access): 1 - nonirradiated; 2 - 10 Mrad; 3 - 20 Mrad; 4 - 40 Mrad.

The results of the study of the influence of neutron ($2 \cdot 10^{18}$ neutron/cm^2) and electron (40 Mrad) irradiation on the dielectric characteristics of polyethylene of low and high density are given very comprehensively in work [342]. The analysis of the data confirms that the increase in the value of tg δ with an increase of irradiation dose is conditioned by the process of radiation oxidation.

A study was made of the influence of ionizing radiation on the electrical properties of fine films made from high-density polyethylene [343]. It was established that the tg δ of polyethylene (at a frequency of 1 MHz) in the initial state depends weakly on temperature over the range of 20-140°C, however, with an increase in the irradiation dose its absolute value increases and the temperature dependence becomes more acute.

The results of the investigation of the dependence of electrical strength on temperature at various doses of irradiation confirmed the conclusions made in work [336].

The volume resistivity of irradiated (0-300 Mrad) films made from high-density polethylene is changed nonmonotonically with an increase of temperature and in the interval of 90-120°C a minimum is observed, the value of which is greater the higher the exposure dose. It is characteristic that for samples which after irradiation are subjected to heating at 140°C for 5 min there are no such minima. Such a one-time surge of electrical conductivity into the area of temperatures close to the melting of crystals can be connected with the release of the charge carriers from the traps where they were trapped in the process of irradiation.

A study of the electrical resistance of irradiated polyethylene in water under the joint influence of temperature (up to 250°C) and pressure (up to 1200 kgf/cm^2) has been carried out in work [344].

In this case it was established that the insulation resistance remains above 1.5 10^{10} $\Omega \cdot$cm under the joint influence of a temperature of 170-180°C and pressure greater than 1000 kgf/cm^2.

Some data on the change in the dielectric properties of polyethylene depending on the conditions of irradiation and dose are given in works [317, 345] and confirm the regularities given above.

The properties of polyethylene irradiated in the presence of sensitizers of radiation cross-linking. In work [273] a study is made of the influence of sensitizers (allyl methacrylate, divinylbenzene, diallyl malleate) on the physicomechanical and electrophysical properties of irradiated polyethylene of low (Marlex 1762) and high (Marlex 6009) density.

In the case of the irradiation of polyethylene with an additive of a polyfunctional monomer in a dose of 8 Mrad a higher value of strength at break (350 kgf/cm^2) is attained than during the irradiation of polyethylene without the monomer up to a dose of 64 Mrad (250-290 kgf/cm^2). The strength characteristics of polyethylene at room temperature, as also at temperatures higher than the melting point, also prove to be significantly higher if irradiation is conducted in the presence of a polyfunctional monomer . The strength of low-density polyethylene at a temperature of 115°C comprises ∿20 kgf/cm^2, if it has been irradiated in the presence of allyl methacrylate, and only 7 kgf/cm^2 if irradiation is conducted with the addition of a sensitizer. This distinctly shows that in the absence of crystallinity the strength of a polymer at a temperature higher than the melting point is determined by the three-dimensional network formed because of the cross-linking of the molecules of polyethylene in the presence of a polyfunctional monomer.

The dielectric characteristics of polyethylene irradiated in the presence of sensitizers are given in Table 21.

Table 21. The change in the electrophysical characteristics of polyethylene during irradiation.

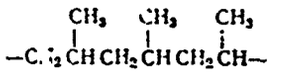
Polyethylene	Conditions of irradiation		Dielectric permeability		$tg\ \delta \cdot 10^4$		Monomer
	dose, Mrad	source	1 kHz	1 MHz	1 kHz	1 MHz	
High density	0—37	accel-erator	2,34—2,39	2,33—2,40	1	1	Is absent
	1—8	Co^{60}	2,34—2,35	2,34—2,35	2—3	4—7	"
	1—8	Co^{60}	2,34—2,37	2,33—2,38	3—9	4—8	Allyl methacrylate
	1—8	Co^{60}	2,35—2,37	2,36—2,28	2—3	4—7	Divinylbenzene
	1—8	Co^{60}	2,34—2,38	2,33—2,36	3—4	4	Diallyl malleate
Low density	0—37	accel-erator	2,27—2,28	2,27—2,29	1	1	Is absent
	1—8	Co^{60}	2,29—2,31	2 29—2,30	3	4	"
	1—8	Co^{60}	2,27—2,30	2,26—2,33	7—18	5—9	Allyl methacrylate
	1—8	Co^{60}	2,27—2,33	2,27—2,33	3	4	Divinylbenzene
	1—8	Co^{60}	2,28—2,32	2,27—2,30	4	4	Diallyl malleate

From the data in the table it is evident that the introduction of a monomer insignificantly influences the dielectric characteristics of irradiated polyethylene, whereupon the greatest contribution to change is made by allyl methacrylate as the most polar of all the tested monomers.

It is evident that the use of sensitizers for obtaining the required effect of cross-linking at small doses will not entail a deterioration of properties of irradiated polyethylene; the latter can be used even as high-frequency electrical insulation.

Polypropylene

This material, which in structure occupies an intermediate position between polyethylene and polyisobutylene, can be considered as a polymer obtained from polyethylene by means of the replacement of the atoms of hydrogen at the alternated atoms of carbon by methyl groups



Isotactic polypropylene possesses a higher degree of crystallinity and has a higher melting point and temperature of vitrification.

Polypropylene also relates to the class of cross-linked polymers, i.e., during irradiation cross bonds are formed in it, however, this process flows with less probability than in polyethylene (relationship of the rates of the processes of degradation and cross-linking comprises 0.6-0.8) [99]. The gases being liberated during irradiation almost wholly (99%) consist of hydrogen [346]. Data on the change in electroconductivity during or after irradiation are lacking in the literature.

The tear resistance of polypropylene irradiated in an inert medium and measured at 60°C barely changes up to a dose of 160 Mrad, however, at 20°C tear resistance along with an increase in irradiation dose at first increases and reaches a maximum at 80 Mrad, and then it diminishes and at a dose of 160 Mrad reaches its original value. The strength of polypropylene fiber with an increase in irradiation dose diminishes and at a dose of 150 Mrad comprises 40% from the strength of the initial fiber. The breaking strain of polypropylene fiber also decreases with an increase in the irradiation dose [347].

In work [348] it was revealed that in contrast to polyethylene during irradiation up to a dose of $2.2 \cdot 10^7$ rad in isotactic polypropylene sharp changes occur. The polymer became brittle, changed color, and strength at break was strongly decreased. At higher doses the polymer became soft and its elongation began to be lowered to zero, which is attributed to the plasticizing action of the low-modular fraction which is formed during radiation degradation. During irradiation up to a dose of $1 \cdot 10^9$ rad the surface of the polymer became oily due to further degradation.

On the other hand, in work [349] they noted that polypropylene irradiated at room temperature up to a dose of $4 \cdot 10^7$ rad and immediately annealed at a temperatures between 120 and 260°C remains pliable and retains a noticeable value of elongation. It has also been shown that many properties of polypropylene depend on the temperature of irradiation. With a thorough selection of temperature and conditions of annealing after irradiation it is possible to obtain a cross-linked, sufficiently pliable polypropylene. If these conditions are not observed degradation strongly influences the physical properties of the polymer during irradiation already up to relatively low doses.

In work [350] it was shown that the thermal stability of polypropylene is sharply lowered with an increase of irradiation dose.

The Copolymer of Ethylene with Propylene

The copolymer of ethylene with propylene [351] is a high-molecular product of the joint polymerization of the indicated monomers and basically has the following structure:

$$CH_3-CH_2-(CH_2-CH_2)_n-(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}})_m-CH=CH_2$$

With an increase in the content of propylene a disruption of the ordered packing of the polymer chains is observed. Gradually the degree of crystallinity and density are lowered.

The investigation of the radiation cross-linking of polyolefins showed [251] that this copolymer belongs to the group of cross-linked polymers, whereupon a characteristic for it is less value of the relationship of the rates of degradation and cross-linking (β/α = 0.12-0.20) than for polyethylene.

The strength characteristics of the copolymer of ethylene with propylene are substantially higher than for low-density polyethylene. Therefore during irradiation the lowering of them with an increase of dose occurs approximately at the same rate as in polyethylene, but the absolute values of deformation characteristics at identical doses in the copolymer of ethylene with propylene are higher than in the polyethylene of low density.

The authors of work [255] studied the dependence of the deformation characteristics of this material at various doses of

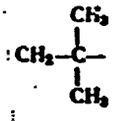
irradiation and investigated the possibility of its thermal stabilization for prolonged utilization in an irradiated form at increased temperatures. Data on the aging of the irradiated copolymer of ethylene with propylene containing 0.5% standard stabilizer (control), and also on the effective heat-stabilizing system, are given below (the criterion of loss of efficiency is taken as the lowering in relative elongation to 100%):

T, °C	Control, hr	Copolymer with thermal stabilizer, hr
150	100-150	4000-5000
175	10-15	700-900
200	1-2	75-175

Apparently this material is very promising for obtaining thermoresistant insulation with the help of irradiation.

Polyisobutylene

This polymer as a result of a peculiarity of the main chain contains a quaternary atom of carbon



degrades during irradiation [352]. Breaks of the main chain are connected directly with the decrease in the value of the number-average molecular weight. Besides the breaks in the main chain, in polyisobutylene during irradiation there is an increase in the content of nonsaturation mainly of the vinylidene type (in the side groups).

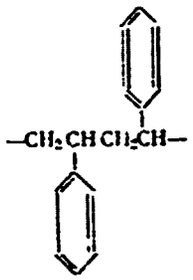
The composition of gases which are liberated during irradiation includes mainly hydrogen, methane, and isobutylene.

The degree of degradation of polyisobutylene during irradiation increases with an increase in temperature.

It has been established that the copolymers of isobutylene and styrene are less subjected to degradation than polyisobutylene itself.

Polystyrene

This polymer can be considered as a material obtained from polyethylene by the replacement of the atoms of hydrogen at the alternated atoms of carbon by phenyl groups



During the action of ionizing radiations on polystyrene the predominant effect is cross-linking, although the measurement of the content of sol fraction made it possible to uncover that degradation in it nevertheless flows, true to an insignificant degree [108, 353]. During irradiation in the air the degree of degradation probably depends on the thickness of the sample and the dose rate.

As established in work [105], the main chain of the polymer apparently participates both in the process of liberation of hydrogen and in cross-linking, which is accomplished through the benzene ring with the interrupting of double bonds in the aromatic grouping.

The physicomechanical properties of polystyrene during irradiation are changed very little. Thus in unmodified polystyrene the tensile strength and tear resistance are decreased all told only by 5-10% during irradiation up to a dose of $5 \cdot 10^9$ rad. Polystyrene containing an additive (for instance a plastifier) is more susceptible to the effect of ionizing radiations; true its strength does not diminish during irradiation up to very high doses, however, the relative elongation drops noticeably already at doses of about 10 Mrad.

Polystyrene possesses high radiation stability not only in physicomechanical, but also in electrophysical characteristics. Thus according to works [354, 355], after irradiation up to a dose of 3600 Mrad the volumetric specific resistance practically did not change as compared with the original value ($1 \cdot 10^{14}$ Ω·cm), and dielectric strength was lowered from 64 to all told only 52 kW/mm.

Figure 25 [356] shows the dependence of ε and tg δ on the irradiation dose in a reactor in air at 35°C for polystyrene and polyethylene. It is evident that although change of tg δ for polyethylene is small, for polystyrene it is still considerably less.

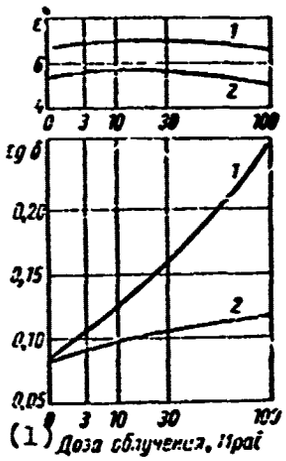


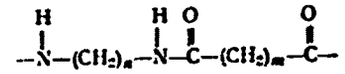
Fig. 25. Dependence of ε and tg δ at 50 Hz and 23°C on the irradiation dose for polyethylene (1) and polystyrene (2).
KEY: (1) Irradiation dose, Mrad.

Some data on the change in the electrophysical characteristics of polystyrene during irradiation in a vacuum are given in work [345].

The Nitrogen-Containing Polymers (the Polyamides)

Nylon

For polyamides the following structure is characteristic:



The melting point of polyamides is higher than for polyethylene as a result of the strong intermolecular interaction at the sites of disposition of amido groups. Polar amido groups represent precisely those places, in which intermolecular chains are attracted to each other by hydrogen bonds; as a result the solubility of polyamides in polar solvents and the equilibrium content of moisture in them prove to be significantly higher than in polyethylene.

During the irradiation of polyamides by ionizing radiation the relationship of the rates of the processes of degradation and cross-linking has a somewhat greater value than in polyethylene; however, qualitatively the initial changes in physicomechanical properties of both polymers are very similar. In contrast to the behavior of polyethylene, with an increase in the irradiation dose the increase of rubber-like elasticity in polyamides at high temperature is gradually slowed down during the transition into the range of high doses [357]. As shown in work [358] degradation occurs as a result of breaking of N–C bonds.

Although in polyamides, as also in polyethylene, there are three basic forms of radiation changes (an increase in the amorphous phase content as a result of the destruction of

of crystalline structure, the formation of defects inside the crystallites, and the formation of a woven network), the most sharply defined change is the increase in hardness as a result of cross-linking. The higher value of the relationship of the probabilities of processes of degradation and cross-linking in nylon determines its lesser radiation stability, if we evaluate it according to the capacity of the material to preserve the original values of strength at breaking and relative elongation.

Data on the other nitrogen-containing polymers, for example aniline-formaldehyde resins are very incomplete. Some of them are given below in composite tables.

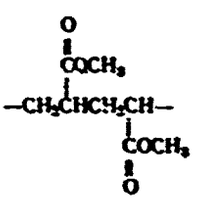
Oxygen-Containing Polymers

The properties of oxygen-containing polymeric materials, depending on the individual features of the compound, are changed in very wide limits.

The different nature of molecular structure also contains their completely different behavior under the action of ionizing radiations.

Polyacrylates

The polyacrylates are derivative of acrylic acid $H_2C=\underset{H}{\overset{|}{C}}-\underset{O}{\overset{\|}{C}}OH$ and the simplest of them - polymethyl acrylate - has the following structure:



The greater part of the investigations of radiolysis of polyacrylates was directed at the clarification of the influence of differences in the structure of the side chain, which represents different ester groups, on the rate of the processes of cross-linking and degradation which proceed under the action of ionizing radiation [359, 360].

Investigation of the influence of ionizing radiations on the structural and physicomechanical properties of polyacrylates was accomplished on rubber-like polymers which are included in the composition of some industrial rubbers. The degree of cross-linking of polyacrylic rubber increases at a greater rate than natural.

Polymethacrylates

In contrast to the majority of widely used polymeric materials, which during irradiation are cross-linked, polymethacrylates undergo degradation. This fact has been confirmed by the numerous fundamental works carried out with the polymer of the simplest ester - polymethyl methacrylate [81, 84, 108]. At the same time the investigation of polymethacrylates with side groups of different structure showed [361] that radiolysis of compounds of this class can to a certain extent depend on the structure of the side chain of the polymer, whereupon the peculiarities of structure predetermine the course of one of the following three processes: the side chain can "exhaust" the absorbed energy on itself if aromatic groupings are present in it; bulky side chains increase steric strains and can facilitate the flow of degradations; finally long side chains can condition the appearance of cross-linked sections.

It has been established that the rate of degradation substantially depends on the presence of additives [81, 102, 362]

regardless of whether they were introduced for the purpose of radiation protection of the polymer or they were present because of other reasons. On the basis of the results obtained (see Table 22) the coefficients of protection were calculated.

Table 22. Protective action of additives during the radiolysis of polymethyl methacrylate.

Additive	Concentration, wt. %	Protection coefficient, %	Additive	Concentration, wt. %	Protection coefficient, %
Benzoic acid	1.0	76	8-Hydroxyquinoline	2.0	52
Naphthalene	2 0	32	Diphenylthiourea	3.6	69
Anthracene	2.1	37			
Phenanthrene	2.2	51	α-Naphthol	5.6	82
Diphenyl	2.5	56	β-Naphthol	5.3	24
Phenol	2.7	52	Ethyl urea	10.0	12
α-Naphthylamine	2.5	78	Paraffin	10.0	3

It is evident from Table 22 that all the most effective protective additives are compounds containing aromatic groupings.

The optical and electric properties of polymethyl methacrylate after irradiation suffer noticeable changes, which is important for some concrete cases of application. For instance, optical transparency during irradiation by γ-radiation in air up to a dose of 5 Mrad is lowered from 90 to 55% [366]. The electrical properties of polymethyl methacrylate were studied both during and after irradiation [364, 365]. It was established that induced conductivity was changed proportional to $J^{0.55}$, where J – the incident radiation intensity. After termination of irradiation conductivity diminished exponentially for a time of more than 5 hours. At a dose rate of 400 rad/hr electroconductivity comprised 10^{-17} $\Omega^{-1} \cdot cm^{-1}$ and had a purely ohmic nature. After

irradiation up to a dose of 5 Mrad electroconductivity was lowered to the original value, although for the extent of a prolonged time; after irradiation up to a dose of 100 Mrad electroconductivity comprised 10^{-14} $\Omega^{-1} \cdot cm^{-1}$.

In work [366] dependences are given for ε and tg δ of polymethyl methacrylate at a frequency of 50 Hz on the dose of reactor radiation at a temperature of 25°C. It has been established that the dielectric characteristics of this material did not undergo substantial changes and its efficiency in the zone of action of ionizing radiations is determined wholly by physicomechanical properties.

The physicomechanical properties of polymethyl methacrylate deteriorate very rapidly during irradiation, which is conditioned by the large number of breaks of the main chain of polymer molecules at a given amount of absorbed energy.

The radiolysis of polymethyl methacrylate is accompanied by intensive gas liberation, whereas the gas (44.1% hydrogen, 22.8% carbon monoxide, 18.8% carbon dioxide, and 6% methane [81]) remains in the polymer and in no way displays itself. During subsequent heating to a temperature above 125°C the almost instantaneous foaming of the polymer occurs.

Polyvinyl Alcohol and Its Derivatives

Polyvinyl alcohol is soluble in water (a unique property of a polymer!). During irradiation in aqueous solutions it is cross-linked [367], whereas irradiation in a dry state both in air and in a vacuum gives rise to degradation [368].

Data on the influence of ionizing radiations on the physicomechanical properties of polyvinyl alcohol are absent in the literature.

Polyvinly acetate was investigated in radiation fields only in the form of copolymers with vinyl chloride and in mixtures with a high content of fillers, therefore on the basis of these works it is impossible to determine which process was dominant: cross-linking or degradation.

Questions on the effect of radiation on the simple esters of polyvinyl alcohol have been treated in few works; these compounds figure in that group of polymers in which during irradiation by electrons a gel fraction is formed [80].

Polyvinyl acetals are used quite extensively in various areas of technology, however their radiation stability also has not been studied sufficiently.

Polyvinyl formal and polyvinyl butyral were investigated after irradiation in a reactor with a limited air inlet. At an exposure dose of 500 Mrad the modulus of elasticity and tensile strength of polyvinyl formal was lowered by approximately 50% from initial [181, 369, 370]; in this range of doses relative elongation, traversing the maximum, increased by more than 50% which attests to the considerable degradation of material.

The changes revealed after irradiation for polyvinyl butyral clearly indicate the preferential flow of the process of cross-linking. The density of this material increases and the increase in the modulus of elasticity is accompanied by a decrease in relative elongation at break.

Polyethylene Oxide

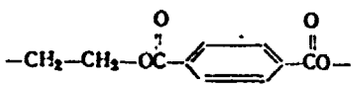
Polyethylene oxide is the only simple polyester about the behavior of which under the action of irradiation a certain quantity of information has been accumulated [371].

The presence of atoms of oxygen in the main chain insignificantly increases the susceptibility to radiation of polyethylene oxide as compared with polyethylene. Irradiation in air up to moderate doses gives rise to a more marked increase in the viscosity of solutions than irradiation in a vacuum, which is connected with the formation of peroxide cross-linkages. More prolonged irradiation in air gives rise to oxidizing degradation. During irradiation in a vacuum there is approximately four times less cross linking than in polyethylene [372].

Data on the change in physicomechanical properties are absent in the literature.

Polyethylene Terephthalate[1]

This material, having the structure



is used widely in industry. The data on the solubility of irradiated samples attest that the predominant process in polyethylene terephthalate is cross linking [79], probably because of the bond at the aromatic ring. However, the data on the crystallization of this polymer show that both cross-linking and degradation flow fairly slowly.

The analysis of infrared spectra showed that the compound ester bond disintegrates; apparently this process represents one of the types of degradation.

Tensile strength, which in the initial state of the material has a higher value than in polyethylene, is reduced to

[1] "Terylene" - in Europe, "Mylar" - in the USA.

50% in the case of an irradiation dose of 500 Mrad and to 10% - with a dose of approximately 2000 Mrad. Based on the degree of change in the original value of tensile strength during irradiation polyethylene terephthalate occupies an intermediate position between polymethyl methacrylate and polyethylene.

The electrophysical (resistance and dielectric strength) and dielectric (ε and tg δ) characteristics of this polyether are not noticeably changed at an irradiation does up to 100 Mrad; with larger doses the gradual deterioration of these parameters is observed [373].

Data are also available for another polyester - Dacron. In work [374] the frequency dependence tg δ is given for Dacron which was not irradiated and for a period of irradiation at a dose rate of 15 r/s. The increase of tg δ and the shift of curves into the range of low frequencies is noticeable, whereupon for crystalline polymer this tendency is expressed more sharply than for amorphous.

Derivatives of Cellulose

During the irradiation of ethylcellulose under such conditions when the presence of air exerts only a small influence a very weak increase was revealed in the modulus of elasticity with a dose of about 40 Mrad [181, 369, 370]. With this dose the tensile strength and impact strength were decreased to 25% from the initial values, and relative elongation - to 5% of the value for nonirradiated material. The decrease in tensile strength by 50% from initial is reached with a dose of 20 Mrad. These data do not give the final answer about the prevalence of cross-linking or degradation.

Cellulose acetate during irradiation behaves in the same manner as ethylcellulose, but for the identical (for instance

50%) decrease in tensile strength somewhat larger irradiation doese are necessary (40 Mrad instead of 20 Mrad). The behavior of cellulose propionate and acetobutyrate during irradiation is not noticeably different from that described above.

The physicomechanical properties of cellulose nitrate during irradiation are changed in much the same manner and to the same degree as the properties of cellulsoe acetate. However, its hardness increases gradually, even in doses greater than 100 Mrad.

As can be seen from the data given above, the simple and compound polyesters of cellulose, and also cellulose nitrate possess a relatively high sensitivity to the action of ionizing radiations similar to that of the initial compound - cellulose itself. The strength characteristics of the derivatives of cellulose deteriorate during irradiation at least 10 times faster than in polyethylene, but nevertheless not as rapidly as in polymethyl methacrylate.

Halogen-Containing Polymers

For the haloid-substituted polymers high yields of radicals during irradiation are characteristic [375, 376]. It has been established that in polyvinyl chloride under the action of radiation changes occur which indicate the flow of reactions both of cross-linking and degradation - depending on the composition of starting material and the conditions of irradiation.

The complete halogenation of a polymer (an example can be polytetrafluoroethylene) gives rise to its degradation at a rapid rate. At intermediate degrees of halogenation predicting the direction of the reaction cannot be done. Thus polyvinylidene chloride undergoes only degradation, whereas

the copolymers of vinylidene chloride and monomers with a higher content of haloids are cross-linked during irradiation.

During the radiolysis of halogenated polymers low-molecular halogen-containing compounds are liberated. The liberated products can enter into an interaction with moisture present in the environment and form ions of halide compounds. Because of this the electrical resistance of such copolymers during irradiation diminishes quite rapidly. Gaseous products regardless of the fact whether they are hydrohalic acids or elementary haloids exert a corrosive action on metals.

Polyvinyl Chloride

This polymer, which has the structure $(-CH_2-CHCl-)_n$, contains 58% chlorine. Unplasticized polymer is used when operating conditions require a high degree of rigidity. If it is desirable to obtain sufficient flexibility and viscosity, then plasticized materials are used.

The effect of light and heat on polyvinyl chloride leads to the liberation of hydrogen chloride and is accompanied by the formation of double bonds.

Irradiation by ionizing radiation also leads to the dehydrochlorination of polyvinyl chloride. It is significant that in this case the influence of stabilizers is expressed considerably less than in the case of the effect of light ahd heat, since the concentration of radicals formed turns out to be many times greater.

The process of HCl loss which takes place during irradiation is accompanied by the formation of double bonds [377], by cross-linking, and by degradation; the radiation yield of double bonds

depends on the temperature of irradiation. At low temperatures solitary double bonds are formed while at room temperature the reaction of dehydrochlorination has a chain nature and as a result systems of linked double bonds are formed. With an increase in the exposure dose approximately up to 800 Mrad at 20°C disappearance of the end double bonds formed during the break of the main chains of the polymer is observed, which is apparently [375, 377] connected with the onset of linked systems and the formation of cycles. The degree of degradation is less during irradiation in a vacuum than in air [378, 379]. The radiochemical yield of the process of cross-linking of polyvinyl chloride turns out to be greater during irradiation of the polymer in certain solvents than in a solid state.

The influence of ionizing radiation on the plasticized formula of polyvinyl chloride has the same nature as the influence on solutions [380]. During irradiation in air [381] in an unplasticized polymer degradation takes place to a greater degree, which is apparently connected with the difficulty of the recombination of polymeric radicals in a more rigid unplasticized material. In addition it was revealed that plasticizers, especially tricresyl phosphate and phenyl decresyl phosphate, exert a protective action on polyvinyl chloride during irradiation [381].

Upon the introduction of unsaturated monomers of compound polyesters into the formula the yield of cross-linking increases [301]. It has been found [382] that the addition to polyvinyl chloride of triallyl ester of cyanuric acid (triallyl cyanurate) sharply lowers the irradiation dose for obtaining material with a higher thermal stability and resistance to the effect of solvents. For instance, heat resistance in the Vicat test of a mixture of 60 parts by weight of polyvinyl chloride and 40 parts by weight of triallyl cyanurate after irradiation up to a dose of

4 Mrad comprised 160°C while the heat resistance of polyvinyl chloride itself after irradiation remained unchanged (95°C). The irradiation doses which cause the formation of an insoluble fraction comprise correspondingly for polyvinyl chloride and a mixture of polyvinyl chloride (90 parts by weight) with triallyl cyanurate (10 parts by weight) 30 and 0.5 Mrad.

Tensile strength of unplasticized resins diminishes slightly with an irradiation dose up to 100 Mrad; with an increase in the irradiation dose up to 200 Mrad strength diminishes by one third. Impact strength diminishes still more slowly [181, 369, 370, 383]. The dynamic mechanical properties of irridated polyvinyl chloride have been studied [384].

Some plasticized formulas become more solid during irradiation and their modulus of elasticity increases [181, 369, 370], whereas the relative change in tensile strength occurs just as in unplasticized resins. Other compositions are more sensitive, at least by an order of magnitude.

During the irradiation of polyvinyl chloride, plasticized with di(2-ethylhexyl)phthalate, by γ-radiation (dose rate 4 Mrad/hr) in the presence of various stabilizers the tensile strength and relative elongation monotonically diminish, whereupon in a dose of 78 Mrad they comprise approximately half of the original value; the content of gel fraction in this case reaches 55%. The magnitude of 100% modulus and chlorine content diminish by several percent. The molecular weight of the soluble component of the polymer with an increase in irradiation dose traverses the maximum at 33 Mrad, and then it is lowered. Substantial differences in the action of different stabilizers were not detected [385]. In the presence of $CaCO_3$ the more effective filler turns out to be a tin-containing stabilizer as compared with cadmium and barium compounds [386].

It has been established that the heat reistance and resistance to solvents of polyvinyl chloride can be increased by irradiation in water up to doses of 13-1000 Mrad [387-389].

The irradiation of polyvinyl chloride in the presence of NH_3 leads to the formation of a gel fraction to the extent of 93% in a dose of 5 Mrad, whereupon the nitrogen-containing polyvinyl chloride possesses a different reactivity, moisture absorbtion, and shade [390].

For the cross-linking of polyvinyl chloride it is also proposed to conduct irradiation in an atmosphere of inert gas or in a vacuum, and then heating in this atmosphere up to 80-150°C [391].

For an improvement in the physical properties of polyvinyl chloride and its copolymer it is recommended to introduce mineral fillers (soot, SiO_2, kaolin with particle sizes 20-50 nm) to the extent of 0.05-7 parts by weight per 100 parts by weight of polyvinyl chloride, and then to irradiate up to 5-25 Mrad. The composition can include stabilizers, plasticizers, and other components. The products obtained by such a method possess higher mechanical properties than nonirradiated polyvinyl chloride with a filler and irradiated polyvinyl chloride without a filler [386, 392].

For obtaining a thermo- and cold-resistant product it is suggested to introduce into polyvinyl chloride (to the extent of from 1 to 50% of the weight of the polymer) substances which contain many epoxy groups and to irradiate this composition up to a dose of 5-50 Mrad [393].

Improvements in the physical properties of polyvinyl chloride and its copolymers can be attained by introducing into ..e

composition a composition of 1-50 parts by weight of magnesium oxide or 1-4 parts by weight of the stearate of an alkali metal per 100 parts by weight of polymer and irradiating them to a dose of 100 Mrad [394].

The electrical characteristics of plasticized polyvinyl chloride resins deteriorate rapidly during irradiation. The specific volumetric electrical resistance of the copolymer of vinyl chloride with vinyl acetate after irradiation up to a dose of 100 Mrad fell below 10^6 Ω·cm [181, 369, 370].

In work [395] a detailed investigation is made of the change in the physicomechanical and electrophysical properties of the polyvinyl chloride masticated rubbers of insulation and hose formulas, the composition of which is given in Table 23.

Table 23. Composition of the formula of polyvinyl chloride masticated rubbers.

Components	Insulation						Hose	
	Number of formula						Number of formula	
	230	251	224	489	1011	38	239	289
Polyvinyl chloride	100	100	100	100	100	100	100	100
ED-242 (plasticizer)	45—47	-	30	-	-	-	50	-
Dioctyl phthalate	-	52—55	-	-	47—50	-	-	60
Dioctyl sebacate	-	-	-	28	-	-	-	-
Tricresyl phosphate	-	-	10	5	-	-	10	10
Dibutyl phthalate	-	-	-	-	-	35	-	-
Diphenyl chloride	-	-	-	-	-	20	-	-
Lead silicate	12	12	15	-	-	-	15	-
White lead	-	-	-	10	-	-	-	-
Blue pigment	-	-	-	-	-	-	0.7	-
Calcium stearate	3	3	3	3	3	3	3	-

It has been established that tensile strength is noticeably lowered in the interval of doses of 5-50 Mrad, and relative elongation drops monotonically in all the investigated range of doses. A sharper change in strength characteristics is revealed for the formulas of masticated rubbers with a high content of plasticizers.

Specific volumetric resistance is lowered very sharply with an increase in irradiation dose and at 150 Mrad comprises from 3 to 37% (depending on the composition of formula) of the original.

Within certain limits there are also changes in the ε and tg δ of masticated rubbers.

The study of the change in freeze resistance (the loss of plasticity at bend of 180° around a rod with a diameter of 1 mm) and the decomposition temperatures of polyvinyl chloride masticated rubber (the liberation of HCl) during irradiation showed that freeze resistance sharply, and decomposition temperature more smoothly are lowered at doses of irradiation greater than 15 Mrad.

The moisture pick-up of masticated rubbers increases noticeably over the range of doses 1-40 Mrad, which is apparently connected with the formation of polar groups as a result of the oxidation processes which proceed under the action of ionizing radiation in the presence of atmospheric oxygen.

The copolymers of vinylidene chloride and vinyl chloride (firm name "Saran") are similar to the polymers of vinly chloride and vinyl acetate, but they are somewhat more pliable and softer. The prevailing process in them is the degradation of macromolecular chains. At an irradiation dose of about 50 Mrad the modulus of elasticity diminishes by 25%, and tensile strength

is still more; electrical resistance during irradiation diminishes rapidly.

Fluorine-Containing Polymers

Polytetrafluoroethylene $(-CF_2-CF_2-)_n$, polytrifluorochloroethylene $(-CF_2-CFCl-)_n$, and polytrifluoroethylene $(-CF_2-CFH-)_n$ possess high heat resistance and chemical inertness. At the same time these polymers are completely inclined to degradation under the action of ionizing radiations [396-399]. Destruction is accompanied by the liberation of the corrosive products.

The investigation of polytetrafluoroethylene by the [EPR] (ЭПР) method showed that the primary free radicals formed during irradiation in a vacuum in the case of irradiation in the presence of air enter into a reaction and form peroxide type radicals [400, 401]. By the method of infrared spectrometry and by the measurement of density it has been established that during irradiation up to small doses the degree of crystallinity of polytetrafluoroethylene increases [402]. Roentgenographic studies of irradiated polytetrafluoroethylene and polytrifluoroethylene [403] also confirmed the increase of crystallinity in polytetrafluoroethylene. This is connected with the breakings of chains in the amorphous phase. At doses above 300 Mrad a decrease of crystallinity is observed. In polytrifluoroethylene the decrease in crystallinity was observed at doses above 200 Mrad.

The rate of degradation during irradiation in a vacuum is an order of magnitude less than in air. The influence of the medium during the irradiation of polytetrafluoroethylene and polytrifluoroethylene is more significant than during the irradiation of other polymers; upon contact with air the surface layers of these two materials can be oxidized [404]. Such a surface

oxidation improves the capacity of polytetrafluoroethylene for coloration and grafting on the surface of other monomers. The radiochemical yield of the process of degradation of polytetrafluoroethylene during irradiation in air is several times greater than for polyvinyl chloride [405]. The behavior of polytrifluorochloroethylene is the same. During irradiation in the presence of air polymer density and the viscosity of fusion increase [406]. In spite of high thermal stability, polytetrafluoroethylene and polytrifluorochloroethylene are most susceptible to the effect of radiation in the presence of air. Fluorine-containing polymers which are not completely halogenated can be cross-linked during irradiation.

The irradiation of polytrifluoroethylene in a vacuum by γ-radiation over the range of 1 to 200 Mrad showed that in this case both cross-linking and degradation take place, and $\beta/\alpha = 0.14$. During irradiation branched structures are formed which are thermally less stable than the initial polymer [407, 408].

During irradiation in air the physicomechanical characteristics of these polymers deteriorate rapidly. Tensile strength of the samples of polytetrafluoroethylene after irradiation up to a dose of about 4 Mrad was cut in half; relative elongation was cut in half at a still lower irradiation dose - a total of 2 Mrad. After such a sharp lowering strength continues to decrease with an increase in irradiation dose, but less sharply and comprises an additional 29% of original value at an irradiation dose of about 60 Mrad.

Radiation stability of polytrifluorochloroethylene is somewhat higher than polytetrafluoroethylene; tensile strength of polytrifluorochloroethylene was lowered to half of the original value at doses of about 30 Mrad, and with further irradiation the drop in strength occurred very sharply.

The data cited above relate to thick (about 5 mm) samples which were being irradiated in air at a dose rate of 10^6 rad/hr.

Since fluorine-containing polymers are very sensitive to the presence of oxygen in the process of irradiation, one ought to take into account that for samples of lesser thickness the strength characteristics will deteriorate still more sharply.

Figure 26 shows the dependence of the electrical conductivity of polytetrafluoroethylene on temperatures during irradiation by γ-radiation of Co^{60} (dose rate 15 r/s). It is evident that with the entry of this material into the radiation zone its conductivity will increase sharply whereupon at a temperature of ∿30°C the absolute value of electrical conductivity during irradiation will increase approximately 100 times as compared with initial.

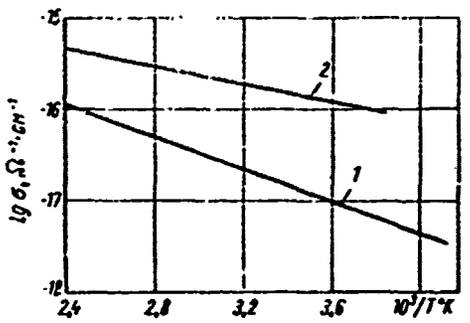


Fig. 26. The dependence of electroconductivity of polytetrafluoroethylene on temperature before (1) and during (2) irradiation at a dose rate of 15 r/s.

The dielectric characteristics of halogen-containing polymers are changed relatively weakly during irradiation and the determining factor is the loss of mechanical strength, and not the deterioration of electrophysical properties.

The investigation of the copolymer of fluoroethylene with ethylene [409] during irradiation by accelerated electrons showed that degradation and cross-linking take place simultaneously, whereas the prevalence of one or the other process depends on the temperature during irradiation: below 80°C degradation predominates and above 80°C the process of cross-linking predominates.

At temperatures above 300°C thermal degradation predominates. Irradiation up to moderate doses does not worsen the capacity of the material for treatment.

During irradiation by γ-radiation of Co^{60} polyvinylidene fluoride is cross-linked [410]. The solubility of the polymer, irradiated up to a dose of 2 Mrad, comprises 74% (26% gel fraction), and after a dose set of 500 Mrad - only 4%. Tensile strength of the irradiated material increases and elongation decreases The differences in behavior under the influence of radiation of such similar materials as polyvinylidene fluoride and polyvinylidene chloride (which degrades under these conditions) are apparently explained by the lesser atomic radius of fluorine in comparison with an atom of chlorine.

The pyrolysis of polyvinyl- and polyvinylidene fluoride, preliminarily irradiated by γ-quanta of Co^{60}, has been studied in work [411]. It has been shown that the presence of hydrogen in monomeric links of fluorine polymers facilitates the formation of cross bonds under the action of γ-radiation. However, although the process of cross-linking is predominant the breaking of chains takes place to a noticeable degree. After irradiation the thermal stability of these polymers is lowered. The increased rate of loss of weight of irradiated polyvinylidene fluoride is not conditioned by the increase in the rate of liberation of HF, but by the change in the structure of the polymer from linear to branched.

The influence of irradiation on the dielectric characteristics (ε, tg δ over a wide range of frequencies - from 100 Hz to 500 kHz) of polytetrafluoroethylene, polytrifluorochloroethylene, and also the copolymer of tetrafluoroethylene and hexafluoropropylene is examined in work [345].

The sharpest changes have been revealed in the behavior of polytetrafluoroethylene. In a dose of 1 Mrad value of tg δ increases by 3 orders at 100 Hz and by 1 order at 100 kHz. With a further increase in irradiation dose the value of tg δ is considerably lowered. The change in the dielectric characteristics of the copolymer of tetrafluoroethylene with hexafluoropropylene is less than for polytetrafluoroethylene, but nevertheless it is completely noticeable, although at somewhat larger irradiation doses (~30-40 Mrad).

Thermoreactive Resins
(Phenolic, Epoxide, Polyester)

The radiation stability of phenol and epoxide resins is approximately identical, but in epoxide resins it can change substantially depending on the hardening agents used. Fine films or coverings from epoxide resins are also subjected more to destruction during irradiation in the presence of oxygen than a film made of phenolic resin [412].

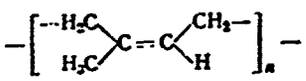
The comparison of epoxide resins hardened by various agents showed that products with higher radiation resistance are obtained by the hardening of the resin with aromatic, and not aliphatic compounds. Irradiation in air at 70°C up to a dose of about 1000 Mrad led to the lowering in bending strength by less than by 40%. There are reports that the chain is degraded near the atom of nitrogen and that the residue of the molecule of epoxide resin is slowly subjected to cross-linking.

Elastomers

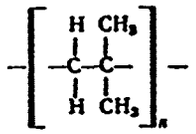
Carbon Chain Compounds

As shown in a number of works [181, 313, 352, 369, 370], the majority of elastomers (with the exception of synthetic rubbers

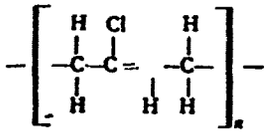
with a large number of links of isobutylene), both natural and synthetic, are cross-linked during the action of ionizing radiations. The majority of studies were carried out with natural rubber - polyisoprene (NR)



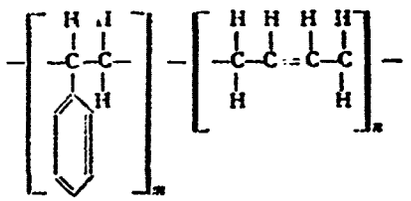
However, there are also reports on synthetic rubbers: the polyisobutylene (IR)



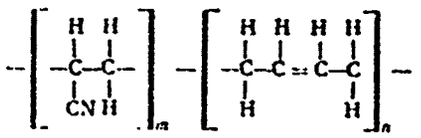
polychloroprene (CR)



the copolymer of butadiene with styrene (SBR)



and the copolymer of butadiene with acrylonitrile (NBR)



The composition of rubber has a significant influence on its behavior during irradiation. For instance, the cross-linking density of copolymers butadiene-styrene diminishes with an increase in the styrene content [414]. Mixtures of natural rubber which are cross-linked during irradiation and butyl rubber, which is degraded, are not radiation-resistant materials, if we judge by tensile strength or by relative elongation [181, 369, 370].

Table 24 shows the changes in the deformation characteristics of four standard (ASTM) rubber mixtures which take place during irradiation [415]; all the mixtures are cross-linked under these conditions.

Table 24. The deterioration of deformation characteristics of rubber mixtures during exposure to ionizing radiation.

Rubber filled with soot	Characteristics	Dose of γ-radiation, Mrad				
		0	9.25	32.4	64.8	92.5
Natural rubber (NR)	Tensile strength, kgf/cm²	427	404	328	211	155
	Elongation at breaking, %	340	290	220	140	60
	Modulus at 100% tension, kgf/cm²	33	37	46	51	56
Butadiene-styrene rubber (SBR)	Tensile strength, kgf/cm²	343	338	314	257	188
	Elongation at breaking, %	370	280	210	150	80
	Modulus at 100% tension, kgf/cm²	23	26	35	45	70
Copolymer of chloroprene with neoprene (CR-GN)	Tensile strength, kgf/cm²	226	200	122	Broken at bend	
	Elongation at breaking, %	180	140	50	The same	
	Modulus at 100% tension, kgf/cm²	35	44		"	
Butadiene-nitrile rubber (NBR)	Tensile strength, kgf/cm²	280	302	260	230	233
	Elongation at breaking, %	300	200	140	70	40
	Modulus at 100% tension, kgf/cm²	28	46	73		

Different physical tests, both static and dynamic, made it possible to arrange the investigated rubber mixtures in the order of decreasing radiation stability in such a sequence; natural rubber, butadiene-styrene rubber, butadiene-nitrile rubber, the copolymer of chloroprene with isoprene.

The silicon organic elastomers which contain phenyl substitutes in high concentration possess high radiation stability in conjunction with good characteristics in the case of thermal aging [416]. However, although the vulcanized mixtures on the basis of high-phenylated silicon-organic elastomers satisfactorily retain the characteristics which were inherent to them in the initial state during heating and irradiation, the values themselves of these initial characteristics are relatively low.

Elastomers on the basis of polyurethane possess very high radiation stability [417]. Such polymers apparently are suitable for exploitation without deterioration of parameters up to irradiation doses of 100 Mrad and higher. They preserve a resistance to cracking under the influence of strains, i.e., they remain very pliable even after irradiation up to such high doses.

During the analysis of the radiation stability of materials, it is convenient to use the concept of the threshold of radiation damage. By the term "25% threshold" is understood the irradiation dose by ionizing radiations which is necessary for deterioration of a given physical property or characteristic of a certain material, having a technical use, by 25% as compared with the original value. In Table 25 for a comparison the values are given of the threshold doses (determined taking into account a 25% change of the most important characteristic from the original value) of a number of typical elastomers and plastics [418]. Furthermore in it the values are given of the relationships of

equivalent threshold doses attained during irradiation by γ-quanta and fast neutrons.

Table 25. The threshold values of radiation damages.

Polymer	Irradiation dose corresponding to a worsening of characteristics by 25%, Mrad	Equivalent ratio n/γ
Natural rubber (NR)	25	7.9
Butadiene-styrene rubber (SBR)	10	7.2
Butadiene-nitrile rubber (NBR)	7	6.4
Neoprene rubber (CR)	6	4.3
Silicon-organic rubber (SE-450)	4	5.2
Butyl rubber (11R)	4	9.1
Acrylic rubber (Hycar PA)	3	5.8
Polyethylene	90	9.0
Polyvinyl chloride	110	3.8
Polyethylene terephthalate	120	3.6

In work [419] an investigation was made of the influence of ionizing radiation directly on various cable designs and also on insulation and hose rubbers subjected to irradiation in the air, in a vacuum, in water at room and at increased temperatures. Insulation and hose rubbers were subject to irradiation both separately and in a duplicated form.

As the test objects the following cables were used: RShM with a section of 200 and 500 mm^2, KVD with a section of 1[illegible] × × 2.5 mm^2 in braid and without it, KNRP with a section of 1 × × 10 mm^2 and 24 × 2.5 mm^2 and others, and also cable rubbers: a) insulation - TS-35 (on the basis of NK and SKB), TSSh-30, NVP-50 (also on the basis of natural and butadiene sodium rubber

filled with chalk and talc); b) hose - ShN-40 (on the basis of chloroprene), ShBM-40 (on the basis of divinyl styrene rubber SKS-30 and butadiene rubber SKBM) and NShP-60 (on the basis of natural and butadiene SKRD rubbers).

It was established that under the influence of irradiation in air the hardness of rubbers progressively increases and relative elongation drops sharply; breaking strength is changed nonmonotonically and depends on the concrete formula of the rubber mixture.

The effects of ionizing radiations on the electric properties of cable rubbers are given in Table 26.

Table 26. The change in the electric properties of insulation rubbers during irradiation in air.

Material	Dose Mrad	ε	tg δ	ρ_v, Ω·cm	E, kV/mm
ShVP-50	0	2,86	0,01	$1,5 \cdot 10^{14}$	28
	50	—	—	$2,06 \cdot 10^{13}$	34
	100	2,85	0,013	$5,9 \cdot 10^{14}$	46
	200	3,86	0,013	$1,3 \cdot 10^{14}$	36
NVP-50 doubled with NShP-60 through a layer of paper	50	4,5	0,086	$9,0 \cdot 10^{12}$	40
TSSh-30	0	3,17	0,013	$7,3 \cdot 10^{14}$	33
	50	4,90	0,056	$1,9 \cdot 10^{14}$	26
	100	4,20	—	$1,5 \cdot 10^{12}$	31
	200	4,80	0,061	$5,2 \cdot 10^{13}$	28
TSSh-30 doubled with ShN-40	50	5,15	0,062	$1,4 \cdot 10^{14}$	24
	100	4,70	0,069	$5,8 \cdot 10^{14}$	30
	200	5,10	0,080	$2,5 \cdot 10^{13}$	23
TSSh-30 doubled with ShN-40 through a layer of paper	50	5,10	0,076	$6,2 \cdot 10^{13}$	27
TS-35	0	3,10	0,016	$5,2 \cdot 10^{13}$	39
	50	3,89	0,056	$1,6 \cdot 10^{13}$	30
	100	4,86	—	$8,2 \cdot 10^{13}$	34
	200	4,50	0,076	$5,9 \cdot 10^{13}$	35
TS-35 doubled with ShBM-40	50	3,90	0,056	$2,2 \cdot 10^{13}$	34
	100	—	0,081	$2,2 \cdot 10^{12}$	33
	200	3,30	0,082	$2,2 \cdot 10^{11}$	35
TS-35 doubled with ShBM-40 through a layer of paper	50	1,50	0,105	$1,3 \cdot 10^{13}$	34

In all cases a worsening of the fundamental electrical insulating properties with an increase of irradiation dose has been noted. Dielectric permeability and the dielectric loss factor increase. Volumetric specific resistance is lowered (rubber TSSh-30). At doses of irradiation greater than 50 Mrad the electrical insulating properties of all investigated rubbers in a number of indices deteriorate significantly. For rubber TS-35 and NKP-50 a lowering in breakdown strength and specific volumetric resistance after irradiation was not detected.

The simultaneous exposure to ionizing radiation and increased temperature deteriorates the physicomechanical properties of cable rubbers more rapidly (Table 27).

Table 27. The influence of the joint action of ionizing radiation and increased temperature on the physicomechanical properties of cable rubbers.*

Material	Temp. in with ir- radia- tion, °C	Dose, Mrad	Indices				
			M	σ	T	L	l
TS-35 (insulation rubber)	18	0	20	69	58	480	37
	70	0	30	92	63	490	48
	100	0	36	83	66	415	50
	18	50	24	50	61	413	63
	70	50	29	49	65	420	64
	100	50	22	27	63	256	24
ShN-6 (hose rubber)	18	0	42	84	76	300	11
	70	0	55	84	84	293	24
	100	0	73	89	84	215	9
	18	50	45	65	85	210	16
	70	50	—	66	80	50	2
	100	50	—	78	88	105	5

*Dose rate 0.7 Mrad/hr, duration of irradiation 70 hr; σ - breaking strength, kgf/cm^2; M - modulus at 100% tension, kgf/cm^2; T - Shore hardness; L - relative elongation, %; l - residual elongation, %.

The results of the testings of the hose rubber, taken directly from irradiated cable products, are given in Table 28.

Table 28. Influence of γ-irradiation on the strength of hose rubbers in cables.*

Brand of cable	Types of rubber	Irradiation dose Mrad	σ	L	l
KVD (hose without braid) with a section 16 × 2.5 mm²	ShN-40	0	68	372	19
		50	59	268	18
		200	52	100	6
KVD (hose over braid)	ShN-40	0	71	336	24
		50	61	265	18
		200	35,6	100	5
KVD (hose under braid)	ShN-40	0	18 .	280	14
		50	11,5	200	12
		200	20	80	3
RShN with a section 200 mm²	ShBM-40	0	38,8	208	13
		50	39	200	9
		200	20	75	4
RShN with a section 800 mm²	NShP-60	0	158	580	14
		50	111	590	18
		200	163	321	15
		350	25,3	175	10

*σ - breaking strength, kgf/cm²; L - relative elongation, %; l - residual elongation, %.

From the preceding information it is evident that after irradiation up to doses higher than 50 Mrad the properties of rubbers deteriorate noticeably and it is already impossible to guarantee the preservation of operating parameters of cable products. Rubberized fabrics completely disintegrate at irradiation doses greater than 100 Mrad.

Dependence of ε and tg δ of some rubbers on the exposure dose in a reactor has been studied in work [366].

Polysulfide and Organic-Silicon Compounds

Polysulfide elastomers are distinguished from carbon chain by a completely different type of bond in the main chain; it consists of a successive series of atoms of sulfur and methylene group (-CH_2-CH_2-S-S-S-S-). The physical properties of these

materials show that the interaction force between polar polysulfide groups is considerably weaker than between amide and polyester groups. Such rubbers undergo degradation already at very moderate doses of irradiation [328]. In contrast to this ethylene-propylene-polysulfide rubbers are cross-linked at comparatively small doses [413]. The changes in properties obtained in other experiments on the irradiation of industrial materials of this types made it possible to assume [420], that cross-linking takes place in them or only very slow degradation, whereupon the conditions of irradiation (temperature, the possibility of access of oxygen, etc.) also exert a definite influence.

An example of the structure of polymers with a high degree of replacement, the main chain of which actually does not contain hydrocarbon bonds, are the polysiloxanes or, as they are frequently called silicon-organic polymers:

$$-O-Si(R_2)-O-Si(R_2)-$$

The radiochemical yield of the cross-linking of methyl siloxane polymers in magnitude was of the same order as for polyethylene [421, 422].

With the exception of silicon-organic polymers, the replacement of atoms of carbon in the main chain by any others gives rise to a lessening of the pure yield of cross-linking. This is probably conditioned by acceleration of the process of degradation. If in the main chain of the polymer the bond is accomplished through groupings containing certain electronegative atoms, as, for example, amide and polysulfide groups, then such a polymer will be definitely more subject to degradation.

Very little data have been published on the radiation stability of electrical insulation on the basis of silicon-organic

systems. In work [423] an investigation is made of the action of nuclear radiations on some electrotechnical products with silicon-organic insulation (electric motors, wires, cables, etc.). The results of testing cable products will be presented in the appropriate section.

THE SPECIFICS OF OPERATION AND EFFICIENCY OF ELECTRICAL INSULATING POLYMERIC MATERIALS IN THE ZONE OF ACTION OF IONIZING RADIATIONS (IN NUCLEAR REACTORS AND OTHER INSTALLATIONS)

General Considerations

Radiation effects in polymers depend not only on the integral irradiation dose and radiation intensity, but also on a whole series of factors which characterize the conditions of irradiation. Therefore during the analysis of the behavior of an electrical insulating polymeric material in the zone of action of ionizing radiation, for example near the nuclear reactor core, it is necessary to take into consideration the entire totality of parameters which characterize the operating conditions; but in this case one cannot consider that the working conditions for the insulation are distinguished from conventional only by the fact that besides the usually acting factors (the medium, temperature, etc.) only the effect of ionizing radiations is added.

The degree of the radiation effect and even the very nature of the effect can depend to a considerable degree on the negligible features of the composition of the material; in this case the temperature dependences of some properties as a result of irradiation can change completely.

Since the structural imperfections caused by radiation at certain temperatures are relocated and irradiation can cause a significant mobility of defects and atoms, temperature has great significance during irradiation. A temperature increase far from always diminishes the degree of radiation effect on some properties of a material.

Therefore when evaluating the specific properties of a material one cannot proceed from the fact that irradiation at a higher temperature has to lessen the radiation effect. Sometimes annealing after irradiation strengthens, and does not diminish the radiation effect.

One ought to keep in mind that the temperature of the irradiated material or product depends not only on the temperature of the medium in which it is located; during irradiation in a reactor with the powerful neutron flux there will be a supplementary warmup as a result of the absorption of intensive γ-radiation accompanying neutron.

The presence of radiation can radically change the properties of the environment in which irradiated product is found. Air at a sufficiently high intensity of radiation is ionized and becomes a conductor. In a reactor during the irradiation of air the formation of ozone was observed [424]. In humid air a binding of atmospheric nitrogen occurred [425] and under the influence of the nitric acid formed the materials were subjected to very intensive corrosion. The neutral medium - nitrogen - ceases to be neutral during irradiation as a result of the formation of chemically very active oxides of nitrogen even when negligible tracks of oxygen are present.

Since nuclear reactors are shut off periodically for maintenance or repair, and also the reloading of nuclear reactor fuel elements, the temperature within the limits of biological shield does not remain constant, it undergoes changes. With a lowering of temperature the condensation of moisture from the air is possible; therefore, along with the fluctuations of temperature the part will be subjected to the variable humidity of the medium.

The efficiency of a part in a nuclear reactor will depend to a specific degree on the radiation spectrum, i.e., the energy flow distribution of rapid and thermal neutrons, and also γ-radiation.

A substantial influence is exerted on the permissible duration of exploitation of a material not only by the integral flux of irradiation, but also the dose rate or intensity of flux. In a number of cases irradiation up to one and the same integral dose leads to a lesser change in properties in an undesirable direction, if the dose rate is great; for instance, during the irradiation of cables with plastic insulation in air the deterioration in characteristics will be less at a greater dose rate than at low because the oxidation process will be expressed less. If the intensity of irradiation is not great, then for ensuring efficiency up to the same integral dose the use of hermetically sealed shells can be required or even the placing of the cable into an inert medium.

One ought to keep in mind that the operating characteristics of a product with electrical insulating polymeric material will be changed during irradiation.

The resistance of electrical insulation on the basis of polymers can diminish during the irradiation of a product intended for electrotechnical application by several orders of magnitude [354], but the importance of this change depends on the purpose of the given product. For instance, in a cable the electroconductivity of insulation depends to a known degree on the polarity of the direct voltage applied between the current-carrying core and the screen. It has been revealed that with a positive polarity of the current-conducting core with respect to the screen conductivity was higher than in the case of reverse polarity. Furthermore, under the influence of intensive

radiation on the insulated conductor between the core and the screen a potential difference is permissible, the magnitude of which depends both on the integral dose of irradiation and on the semiconductor properties of the insulation which appear during irradiation.

Let us examine the basic considerations about the applicability of polymeric materials as insulation for wires, cables, and other electrotechnical and radio engineering products intended for exploitation under conditions of irradiation.

As was noted in the beginning of this section, radiation effects in polymeric materials depend on the integral dose of irradiation and radiation intensity. Therefore it is advantageous to examine in somewhat more detail the influence of both these parameters on the electrophysical characteristics of polymers taking into account the reversible and irreversible effects caused by irradiation.

Reversible Electrophysical Processes

A typical example of a reversible radiation process is the electroconductivity induced by ionizing radiation.

A significant number of works [364, 365, 426-429, 430-432] have been published on the influence of hard electromagnetic (X-ray and γ-radiation) radiation on the electroconductivity of various organic dielectrics. Subsequent works had the goal to establish the mechanism for radiation electroconductivity, however, the information obtained is still insufficiently complete [433].

In the absence of irradiation through a sample of polymer placed between two electrodes a small current flows which is proportional to applied voltage (leakage current or dark current) and is caused by the disorderly thermal excitations of a small share of the valence electrons being thrown over to the levels of conductivity. During irradiation the current increases rapidly (but not instantly). The difference between these currents is called the induced current i_x; the latter is conditioned by the appearance of free electrons and free holes in the bulk of the dielectric under the influence of ionizing radiations [426].

The currents of dark and radiation conductivity increase with an increase of temperature, but differently, which attests to the different mechanism for these forms of conductivity (Fig. 27).

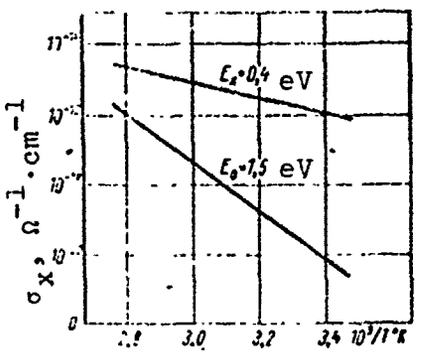


Fig. 27. Temperature dependence σ_x, of activation energy of dark conductivity (E_0) and induced conductivity (E_x) in polyethylene.

At high voltages the currents both of dark and radiation conductivity are proportional to applied voltage, i.e., are subordinated to Ohm's law. Nevertheless there are findings [354] that at low voltages the volt-ampere characteristics bear a nonlinear nature and are similar in form to the characteristics of a crystal rectifier.

At an assigned voltage the current of radiation conductivity i_x depends on the intensity of radiation J according to the following law:

$i_x = kJ^n$, (121)

where k - the proportionality factor; n - exponent, the magnitude of which is changed from 0.5 to 1.0 for various polymers (Table 29).

Table 29. The parameters of induced conductivity of various polymers [434].

Polymer	n	Induced conductivity $(\Omega \cdot cm)^{-1}$ at 20°C and 8 r/s	Decay time of induced conductivity at 20°C
Polymethyl methacrylate (plasticized)	1.0	3×10^{-18}	45 s
Polyethylene terephthalate	0.83	6×10^{-20}	8.5 h
Polyethylene	0.81	9×10^{-17}	7.5 min
Polystyrene	0.65	2×10^{-18}	13 h
Polytetrafluoroethylene	0.63	3×10^{-17}	19 h
Polymethyl methacrylate (unplasticized)	0.55	2×10^{-18}	24 h

The typical dependence of i_x on time during irradiation and after termination of the latter is shown in Fig. 28.

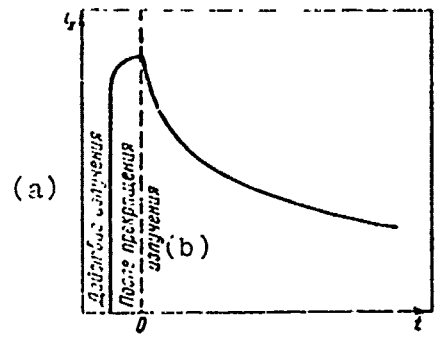


Fig. 28. The dependence of induced current i_x on time t for a polymer subjected to the influence of ionizing radiation. KEY: (a) Effect of radiation; (b) After the termination of radiation.

It is important to emphasize that the reversible effects are determined basically by the intensity of radiation (dose rate) and depend weakly on the integral dose of irradiation (it goes without saying within those limits when the properties of the material still were not changed very strongly as a result of irradiation).

Irreversible Electrophysical Processes

To the number of irreversible processes, along with those noted above in section 1 Chapter III, one should add certain changes in the electrophysical properties of polymers. These changes are important since, on the one hand, polymeric electrical insulating materials can be used as the insulation for cables and other products of electrotechnical application intended for exploitation in nuclear reactors or other apparatuses which are radiation sources and are subjected to irradiation at a low intensity of flow, but for a comparatively long time; on the other hand, irradiated polyethylene (and some other polyolefins) are used as thermoresistant insulation which is subjected to elevated temperatures (150°C and more) for a long time.

A series of investigations [328, 354, 435, 438] made it possible to establish that during irradiation the conductivity of insulation material increases somewhat up to a value determined by the magnitude of the radiation flux intensity. This value remains practically constant in the course of irradiation right up to the beginning of the development of breakdown at a certain saturated absorbed dose, when conductivity again begins to increase. In Table 30 the values are given for the integral neutron fluxes which cause electrical failure for a number of insulation materials.

Table 30. The doses which correspond to the development of spontaneous breakdown.

Polymer	Dose, 10^{18} neutron/cm^2
Polyethylene	10
Polyvinyl formal	2
Polytetrafluoroethylene	5
Polyvinyl chloride	1.9
Silicon-organic rubber	4
Natural rubber	1.3
Polychloroprene	3
Polychlorotrifluoroethylene	1.0

During prolonged irradiation of a dielectric progressively developing process caused by the ionizing radiations begin to be applied to the usual processes of aging and electrical breakdown. Both in the dielectric itself and in the environment (for instance, in air) processes of ionization occur as a result of which leakage currents increase and there is an increase in the probability of surface discharges due to the presence of contaminations. As a result breakdown voltage and the flashover voltage of the insulator across the surface are reduced.

In connection with the low thermal conductivity of insulation and the increased heat evolution due to the leakage currents in the case of direct voltage or dielectric losses with alternating current, which increase as a result of an increase in conductivity with an increase in temperature, thermal equilibrium in the material is disturbed and its temperature is raised.

In polymers in this case supplementary effects appear which are connected with the formation of new ions and free radicals.

These phenomena not only influence electroconductivity during irradiation (reversible effects), but can also entail undesirable irreversible changes in physical and mechanical properties, since they are accompanied by the liberation of various gases (hydrogen, low-molecular hydrocarbons). The internal voids and gas inclusions formed during this weaken the electrical strength of the dielectric and can be the reason for the appearance of internal discharges. In the presence of air (oxygen) the dielectric is oxidized; the polar groupings formed substantially deteriorate the electrical properties of the material.

The contribution of irreversible radiation processes is determined basically by the integral absorbed dose and depends to a considerable extent on the conditions of irradiation (the medium, temperature, and others).

The Efficiency of Electrical Insulating Polymeric Materials Under Conditions of Irradiation

When selecting electrical insulating materials for electrotechnical products which are used in the zone of action of high-energy ionizing radiation it is necessary to take into consideration two fundamental limiting factors: the radiant flux, which considerably shortens the period of service of the products, and the temperature (being defined both by the ambient temperature and radiation warmup), which accelerates the destruction of some polymers or generally preventing the use of others.

The polymers produced today on industrial scales for uninterrupted service directly in a nuclear reactor core are suitable for quite a limited time; this is connected with the fact that in most cases polymers with an acceptable radiation stability are insufficiently thermoresistant, and, on the contrary,

thermoresistant polymers have a very low radiation stability, especially in the presence of oxygen. Near the core, i.e., outside its limits but inside the biological shield, the values of temperature and radiant fluxes are more moderate; therefore, in a number of cases it is possible to use polymeric insulation with a periodic or short-time use, for example in measuring and control cables, and also in the power cables of devices for extraction and reloading of nuclear reactor fuel elements. There are the other uses in which insulation is subjected to irradiation which is beyond the limits of the biological shield of the nuclear reactor or generally outside of a connection with the work of a nuclear reactor, for example wires and cables mounted on powerful isotope radiation sources or on industrial equipment for the processing of nuclear fuel and separation of fission fragments. In these cases both the temperature and flows have still smaller values and it is possible to expect that polymeric insulation will possess a sufficiently prolonged service life.

Table 31 [329] gives the maximum values of temperatures and flows which are characteristic for contemporary power reactors.

Table 31. Temperature and radiation conditions in reactors.

Characteristics	Maximum value	
	In the core	Outside the core
Thermal neutron flux, neutron/($cm^2 \cdot s$)	10^{14}	10^7-10^{10}
Fast neutron flux, neutron/($cm^2 \cdot s$)	2.5×10^{14}	-
Flow of γ-quanta, rad/h	10^6-10^{12}	10^4
Temperature, °C	250-500	100

Before selecting the insulation material which is suitable for exploitation under conditions of irradiation it is desirable to obtain maximally precise information relative to the intensity and the spectral composition of radiation, operating temperature of the installation, temperature and nature of the medium, required parameters of the product (the type of current and voltage, insulation resistance, and others); the minimally permissible service period of the product, the conditions of assembly and exploitation (in the case of cable products - fixed or flexible assembly, uninterrupted or periodic irradiation, etc.). If periodic irradiation is assumed it is necessary to evaluate the number of required cycles of operation. On the strength of this information, and also on the basis of known data on the behavior of various polymeric materials in the zone of action of ionizing radiations, it is possible in most cases to select adequate material for electric insulation. However, in this case it is necessary to introduce sufficient factor of assurance in order to compensate for the uncertainty introduced by calculation in the absorbed doses received by the product because of various components of the reactor radiation which have a complex spectral composition.

Some characteristics for the use in question of properties of a number of polymeric materials are given in Table 32. The temperatures of operation are indicated on the basis of the results of the practical use of these polymers. The maximum permissible doses of irradiation are given in rads. For the characteristics of the last parameter two figures are given: one is based on the results of electrical tests carried out with the fixed assembly of products, and the second corresponds to either a decrease in tensile strength or relative elongation by 50% from the original value. The numerals, based on the results of physicomechanical tests are applicable in cases when the product is subjected to bending during exploitation. In this table data are given on the cross section of capture of thermal neutrons; these figures characterize the degree of induced radioactivity in product after it underwent irradiation by neturons.

Table 32. The characteristic properties of insulation materials.

Insulation	Temperature of operation, °C	Cross section of capture of thermal neutrons, cm^2/g	Maximum dose, rads, according to properties	
			Electrical	Mechanical
Polytetrafluoroethylene	250	0.00077	$2.5 \cdot 10^9$	$2.5 \cdot 10^6$
Copolymer of trifluorochloroethylene and vinylidene fluoride	200	0.1652	$5 \cdot 10^8$	$2.5 \cdot 10^6$
Polyvinyl carbazole	150	0.0115	$5 \cdot 10^9$	$5 \cdot 10^8$
Silicon-organic lacquers	150	0.029	$5 \cdot 10^9$	$2.5 \cdot 10^8$
Epoxide resins	130	-	$5 \cdot 10^9$	$2.5 \cdot 10^9$
Polyvinyl formal	130	0.016	$1 \cdot 10^9$	$5 \cdot 10^8$
Polyvinyl acetate	130	-	$5 \cdot 10^8$	$2.5 \cdot 10^8$
Silicon-organic rubber	125	0.017	$2 \cdot 10^9$	$5 \cdot 10^7$
Polychloroprene	100	0.228	$1.5 \cdot 10^9$	$5 \cdot 10^8$
Polyethylene terephthalate	100	0.008	$5 \cdot 10^8$	$2.5 \cdot 10^8$
Nylon	100	0.029	$5 \cdot 10^8$	$2.5 \cdot 10^8$
Polyethylene	85	0.025	$5 \cdot 10^9$	$2.5 \cdot 10^8$
Polyisobutylene	85	0.030	$5 \cdot 10^8$	$5 \cdot 10^7$
Polyvinyl chloride	85	0.317	$1 \cdot 10^9$	$5 \cdot 10^7$
Natural rubber	85	0.025	$5 \cdot 10^8$	$1 \cdot 10^7$
Butyl rubber	85	0.030	$5 \cdot 10^8$	$5 \cdot 10^7$
Polystyrene	75	0.015	$5 \cdot 10^9$	$5 \cdot 10^8$
Silk natural	70	0.002	$5 \cdot 10^7$	$2.5 \cdot 10^7$
Paper	70	0.002	$5 \cdot 10^7$	$2.5 \cdot 10^7$

When developing cable products intended for exploitation in a nuclear reactor or another similar installation it is necessary to take into consideration a number of specific considerations.

1. *Radiation oxidation.* If the insulation during exploitation is freely exposed to air, then the radiochemical changes in some polymers will be accompanied by oxidation. Such oxidation can be averted by addition into the polymer of special antioxidants, however, even here the protective action is expressed for a limited time. Therefore it is necessary to limit the access of oxygen to the insulation with the aid of a barrier layer, for example in the form of a supplementary plastic protective sheil.

2. *The products of radiolysis which cause corrosion.* Some polymers, for example polyvinyl chloride and polytetrafluoroethylene, during irradiation liberate substances which possess the capacity to cause corrosion; therefore it is not desirable to use them in all cases, with the exception of irradiation by particularly low doses. The small quantities of hydrogen and methane liberated by some polymers (for instance by polyethylene) are harmless, these materials can be used for exploitation in very intensive radiation fields.

3. *Induced radioactivity.* With cables which are subject to irradiation in a reactor sometimes it is necessary to manipulate them for a while, therefore it is desirable that the radioactivity induced in them during irradiation by neutrons be minimum. Generally speaking the basic fraction of induced radioactivity in cable irradiated by neturons is conditioned by the material of current-conducting core and the screening braid, and also by admixtures which are almost always present in all cable materials. Table 33 shows the calculating atomic composition of cable with

polyethylene insulation and a copper tin-plated core and the general radioactivity induced in it is evaluated for a four-week stay in a thermal neutron flux of $\sim 10^{12}$ neutrons/($cm^2 \cdot s$), i.e., after irradiation to an integral flux of $\sim 2.5 \cdot 10^{18}$ neutrons/cm^2.

Table 33. The atomic composition and induced radioactivity in a cable with polyethylene insulation.

Element	Weight per 1 m of cable, g	Activity per 1 m, mCi*		Half-life of the main isotope
		right after irradiation	in two weeks	
C	18.44	Het	Het	-
H	2.998	Het	Het	-
N	0.0009	0.030	0.030	5400 years
Cu	31.272	20.300	Neglible	12.8 h
Sn	0.32	1.75	The same	27 h
Ca	0.00011	0.005	0.004	164 days
Fe	0.00016	0.00016	0.00001	294 years
Pb	0.00003	Neglible	Neglible	-
Ni	0.00019	0.0011	0.00019	256 h
Co	0.00003	0.003	0.003	5.25 years
Ag	0.00006	6.8	0.0006	270 days

*mkyuri (millicurie) - that quantity of any radioactive substance, in which $3.7 \cdot 10^7$ dis/s.

It is evident tnat the activity of an irradiated cable drops quite rapidly in time, if the structural elements or admixtures do not contain isotopes with a large effective cross section of capture of thermal neutrons and an average half-life.

The considerations noted above must be taken into consideration when developing and selecting cable and other products of

Table 34. The radiation stability of insulation polymeric materials.

Class of material	Material	Permissible dose of irradiation, Mrad
Solid molded materials	Diphenyl siloxane reinforced by fiberglass	10,000
	Epoxy-phenol resin with mineral filler	10,000
	Polystyrene	5,000
	Phenolic resins with mineral filler	4,000
Solid molded materials	Epoxide resin reinforced by glass cloth	4,000
	Nylon	2,000
	Polyethylene	2,000
	Polystyrene, impact	2,000
	Phenolic resins with cellulose filler	1,000
	Melamine and urea-formaldehyde resins	1,000
	Nonreinforced phenolic resin	500
	Polyethylene terephthalate	500
	Cellulose acetate	50
	Polymethyl methacrylate	50
	Polytetrafluoroethylene	5
Rubbers and elastomers	Polyvinyl chloride plasticized	500
	Polyurethane	400
	Butadiene-styrene rubber with the addition of antirad	300
	Polyphenylmethylsiloxane	200
	Neoprene	150
	Natural rubber	150
	Polyacrylonitrile	100
	Polysulfide	80
	Polydimethylsiloxane	30
	Polyisobutylene	20
Lacquers	Diphenyl siloxane	5,000
	Aniline-formaldehyde lacquer	5,000
	Vinylcarbazole	4,000
	Composition on the basis of petroleum bitumens	2,000
	Polyurethane	1,000
	On the basis of alkyd resins	500
	On the basis of phenol-formaldehyde resins	500
	Vinyl butyral	400
	Vinyl acetal	400
	Cellulose nitrate	100
	Cellulose butyrate	50
Liquids	Polyphenyls	5,000
	Petroleum oils, radiation resistant	2,000
	Transformer oil (naphthenic)	1,000
	Transformer oil (paraffinic)	500
	Silicone oil	200
Gases	Sulfur hexafluoride	5,000
	Difluorodichloromethane (Freon)	1,000
	Trifluoromonochloroethylene	500
	Perfluoropropylene	100

electrotechnical application intended for exploitation in fields of ionizing radiations in general and in a nuclear reactor in particular.

Table 34 [439, 440] gives the composite data on the change in various properties of plastics and elastomers when exposed to ionizing radiations.

THE BEHAVIOR OF ELECTRICAL INSULATING MATERIALS UNDER THE CONDITIONS OF SPACE

The mastering of space significantly complicated the totality of requirements presented for electrical insulating materials used in airborne cable systems and also in electrical and radio equipment.

The efficiency of space vehicles in orbit depends completely on the normal functioning of electrotechnical and radio-electronic equipment; therefore an analysis of the operating conditions in space, and also the peculiarities of behavior of various polymeric materials under these conditions is of significant interest.

In the solution of technical problems space is understood as the area through which space vehicles have to pass when going into orbit and during the subsequent movement around the earth, and also for the attainment of other celestial bodies. The number of fundamental factors specific for the conditions of space include: 1) vacuum and a vacuum - temperature combination ; 2) ultraviolet radiation; and 3) corpuscular radiation.

The concrete data examined below on the behavior of various materials under these specific conditions are characteristic only for the limited field of space which stretches from the

minimum altitude, at which man-made satellites are launched, i.e., about 200 km and up to the orbits of Venus and Mars. An important feature of this area is its unhomogeneity: the composition of the atmosphere, micrometeorite concentration, the flows of corpuscular radiation are different by ten thousand times. Thus even such a comparatively narrow area of space cannot be described by any specific totality of several most important parameters. Furthermore during the analysis of the properties of materials in space one has to take into account the specific effects conditioned by the spacecraft itself, for example vibration, acceleration, high temperatures, etc.

Finally an important factor which characterizes near space is the presence of the Van Allen belts of the earth, discovered in 1958 during the flights of the third Soviet artificial earth satellite (launched 15 May 1958) and the American satellites "Explorer I" and "Explorer III" [441].

Let us examine consecutively the influence of the fundamental factors which characterize the conditions of space on the behavior of various materials.

Factors Which Characterize The Conditions of Space

Vacuum and a Vacuum - Temperature Combination

A vacuum should be considered as one of the factors of external influence which exerts an evidently expressed gradually showing influence on materials.

In space the vacuum is very high and apparently pressure comprises less than 10^{-12} mm Hg. In proportion to removal from

the surface of the earth pressure is lowered from 10^3 to 10^{-6} mm Hg at an altitude of about 200 km and up to 10^{-12} mm Hg at an altitude greater than 7000 km.

It is known that the stay of materials in a deep vacuum can be significantly expressed on their structure and properties: some materials (for instance some polymers) can decompose under these conditions, whereas others (inorganic compounds and metals) possess the capacity to sublimate. The actual stay of a material in a high vacuum, if it is not accompanied by decomposition, is expressed to a lesser degree on the deterioration of its characteristics than a stay in ordinary atmosphere (corrosion and some other ill effects are absent).

The losses of weight of simple inorganic compounds in a vacuum can be calculated from Langmuir's equation just as for individual elements with the only difference that one ought to take into account the pressure not only of the vapors of the compound itself, but also the gaseous products of its decomposition [442].

The rate of loss of weight of low-molecular organic substances in a vacuum can be calculated by the substitution of the known values of the pressure of their vapors into the Langmuir equation. However, the majority of organic substances used during the preparation of space vehicles are complex high-molecular compounds which upon vaporization do not decompose, but undergo degradation, i.e., the breaking of the main chain of the polymer with the formation of more or less volatile fragments. The molecular weights of such fragments are not accurately established, and for the majority of polymers the values of the decomposition temperatures are known very approximately. Because of the indicated reasons it is not usually possible to use Langmuir's equation relative to polymeric materials and in practical activity

it is necessary to be based on the results of direct experiments for determination of the loss of weight by a sample made of a given material under assigned conditions.

Table 35 [442] gives the values of the temperatures at which the loss of the weight of material in high vacuum comprises 10% a year.

The degradation of organic matter occurs not only in the surface layers of a polymer, but also in its entire volume. The presence of small quantities of admixtures and additives, for example the residues of a catalyst, can considerably accelerate degradation.

A special problem can arise when volatile substances, for example the products of degradation, are subjected simultaneously to the influence of a deep vacuum and significant temperature drops. In this case they can be vaporized from the hot surface and be condensed in the form of an insulating layer on the colder surface, thereby substantially changing the thermal conductivity or the electroconductivity of a part, which disturbs the normal operation of the equipment. When using polymers it is sometimes possible to use protective coatings; they will avert the volatilization of the products of degradation and partly facilitate their recombination.

The loss of weight by polymers in a vacuum can lead to significant changes in properties: physicomechanical, electrophysical, optical, and also to changes in dimensions. It is accepted to assume that a loss of weight by 1-2% still does not cause such changes in properties which would noticeably influence the operating characteristics of the material. However, the loss of weight by 10% already can be accompanied by significant changes in characteristics, and for this very reason such a loss of weight was selected as criterion in the compilation of Table 35.

Table 35. The loss of weight by materials in a high vacuum.

Polymer	Temperature, at which 10% loss of weight a year occurs, °C
Polyacrylonitrile	120
Polybutadiene	250
Rubber NBR (copolymer of butadiene with acrylonitrile)	150-230
Rubber SBR (copolymer of butadiene with styrene)	240
Polycarbonates	180
Cellulose	130
Cellulose acetate	190
Cellulose acetate butyrate	170
Cellulose nitrate	40
Expoxide resins	40-240
Polyesters	40-240
Polyethylene of high density	290
Polyethylene of low density	240-280
Polyethylene terephthalate	200
Polyisobutylene	200
Butyl rubber (copolymer of isobutylene with isoprene)	120
Polyisoprene	190
Melamine resin	190
Polymethyl methacrylate	100-200
Polymethyl acrylate	40-150
Methylphenylsiloxane resin	380
Poly-α-methylstyrene	180-220
Polychloroprene	90
Nylon	30-210
Phenolic resin	130-270
Polypropylene	190-240
Rubber natural	190
Rubber silicon-organic	200
Polystyrene	130-220
Polytetrafluoroethylene	375-380
Polyurethane	70-150
Polyvinyl acetate	160
Polyvinyl alcohol	150
Polyvinyl butyral	80
Polyvinyl chloride	90
Polyvinyl fluoride	270
Copolymer of vinylidene fluoride with hexafluoropropylene	250
Polyvinyl toluene	200

It should be noted that the volatilization of individual components in space flows irreversibly, since in this case the counterpressure which would prevent vaporization does not increase; the vaporized part of substance no longer returns into the initial mass of material.

Ultraviolet (Electromagnetic) Radiation

The electromagnetic radiations which are disseminated in space include radio waves, infrared, ultraviolet, X-ray and γ-radiation. The spectrum of solar radiation in the upper layers of the atmosphere contains an ultraviolet component with a wavelength from 1000 up to 3000 Å, X-radiation with a wavelength from 1 up to 10 Å, and γ-radiation with a wavelength from 0.01 up to 0.1 Å. Precisely these components of electromagnetic radiation are of fundamental interest while the radiant energy of the visible part of the spectrum and especially infrared radiation are transformed into thermal radiation which facilitates development and acceleration of processes of degradation of organic materials which proceed under the action of shortwave radiation.

Electromagnetic radiation noticeably influences only organic electrical insulating materials; inorganic dielectrics and moreso metals are practically insensitive to this form of influence.

During the absorption of ultraviolet radiation by polymeric systems in the high vacuum of space the same processes flow as during the action of ionizing radiation, but with all features inherent to photochemical processes (see p. 30).

To the fraction of ultraviolet radiation it is necessary to attribute on the average of 5% of the total energy of the

spectrum of solar radiation. The terrestrial atmosphere with respect to solar radiation acts as a unique filter, and therefore radiation with a wavelength shorter than 2900 Å practically do not reach the surface of the earth. Exactly that part of the radiation which is filtered out in the upper layers of the atmosphere also causes the greatest damage to materials in space. The quantum energy of radiation with a wavelength of 1000 Å comprises 12.4 eV, 2000 Å - 6.2 eV, and 3000 Å - 4.14 eV. Hence it is apparent that radiation with a wavelength from 1000 up to 2900 Å possesses the greatest energy in the spectrum of ultraviolet radiation, although to it is attributed altogether only 0.2% of all the energy. Knowing that destructive influence which under terrestrial conditions radiation with the greatest wavelength and therefore lesser energy exerts on polymeric materials it is easy to imagine how difficult the operating conditions are for these materials in space.

It has been established that oxygen catalyzes the processes which flow in plastics under the influence of ultraviolet radiation by accelerating degradation. In a vacuum, where oxygen is practically absent, under regulated temperature conditions the processes of decomposition are noticeably retarded. However, in the vacuum of space such a retarding due to the absence of oxygen is not observed as a result of the heating of the material caused by the absorption of infrared rays.

Corpuscular
Radiation

The influence of corpuscular radiation on plastics is developed only when the particles cause a change in material as a result of ionization and excitation. The mechanism for the interaction of high-energy radiation with substance is examined comprehensively in section 1 Chapter I and can be extended completely to the case of corpuscular radiation in space.

THE EFFICIENCY OF ELECTRICAL INSULATING POLYMERIC MATERIALS UNDER THE CONDITIONS OF SPACE

In space insulation materials can be subjected both to direct and to indirect radiation exposure. The greater part of electrotechnical and radio-electronic equipment is disposed inside the spacecraft. Some forms of equipment are placed inside the ship in hermetically sealed sections; here the only factor which complicates the operating conditions of equipment is its heating as a result of heat release. The temperature inside the ship is regulated with the help of the radiating coverings arranged on the outside. Furthermore temperature control is carried out by automatically opening and closing louvers which are triggered during passage of the ship on various sections of orbit which correspond to the minimum and maximum temperatures.

The influence of vacuum on electrical insulating materials as a rule is not catastrophic. In a number of products of gas evolution from plastics usually admixtures are present, for example unreacting monomers and highly volatile products of the main and side reactions, absorbed moisture, gases, and vapors, technical admixtures, for example oils and waxes, and also plasticizers with a high vapor pressure.

The removal of admixtures as a result of gas separation improves the properties of the insulation. Volume resistivity and dielectric strength in this case increase, and the dielectric power factor and dielectric permeability diminish. However, with a temperature increase up to values which correspond to the decomposition temperature of the material all these characteristics are changed in the opposite direction. In the polymer depolymerization and the breaking of chains take place. The products formed

have less molecular weight than the initial polymer and therefore a greater volatility. Therefore the rate of loss of weight and change in dimensions increase while the electrical characteristics gradually deteriorate. Thus for the majority of insulation material a period of stay only in a vacuum still does not exert an ill effect on electrophysical properties, but a combination of the effect of vacuum and temperature will be expressed in a determined manner on the electrical characteristics of the insulation system.

It has been established that some transparent insulation material begin to absorb ultraviolet radiation quite strongly after irradiation for several hours. This leads to the intensive flow of the processes of cross-linking or degradation. In the case of cross-linking electrophysical properties are changed quite weakly and, as a rule, to the side of improvement; if degradation occurs, then the electrical properties are determined by the properties of the newly formed polymer which has less molecular weight than the initial material, and therefore reduced insulating qualities. It is also important to note the following effect: during the absorption of ultraviolet radiation the outer electrons in the molecules can be dislocated. Because of this in short intervals of time, but sufficiently frequently, free radicals or ions can be formed in the material and their presence can condition the appearance of transient electric losses and distort the characteristics of the electron arrangement.

The behavior of thermoplastic electrical insulating materials under conditions of space has been examined in work [443].

The Influence of Vacuum

From the number of thermoplastic materials under conditions of space extensive use is made of nylon and polytetrafluorethylene.

For instance nylon-101 is a stable polymer whose characteristics are barely changed when it is kept in a vacuum at those temperatures which are developed in an orbital satellite. This polymer contains approximately 1% volatile components which are gradually removed. The other admixtures are low-molecular products and absorbed moisture, stabilizers, occluded gases, and vapors. The removal of all these admixtures at temperatures below the decomposition temperature (280°C) actually leads to an improvement in the physicomechanical and electrophysical characteristics of the material. Temperature inside the orbital satellite rarely exceeds 120-150°C, therefore nylon is a very suitable material for use under conditions of space.

Various types of polytetrafluoroethylene are distinguished by the quantities of absorbed moisture, plasticizer, softener, and reagents facilitating processing depending on form, the type of technological procedure for the preparation of material and its processing into a product, thickness, etc. These substances can be volatilized in a vacuum. In such cases the loss of weight to 2% still does not lead to noticeable changes in the dimensions of the part. Under the joint influence of vacuum and temperature a 10% loss of weight per year occurs at 375-380°C. The products of gas evolution are the result of decomposition and depolymerization. Polytetrafluoroethylene can be used under conditions of space, but for a limited duration of stay in the zone of high radiation.

The Influence of Ultraviolet Radiation

Polyethylene becomes brittle during the irradiation by ultraviolet radiation with a wavelength shorter than 4000 Å for several months. Under conditions of space this effect is

accelerated as a result of the fact that the total amount of energy which belongs to the shortwave sector of the spectrum ($\lambda < 4100$ Å) is greater than at the surface of the earth, and therefore brittleness sets in after several days. Polypropylene behaves analogously.

Plasticized polyvinyl chloride after irradiation by ultraviolet radiation with a wavelength less than 4000 Å acquires a stickiness and its surface is discolored. Under conditions of space plasticizers destroy, they are volatilized, and the material becomes brittle with worsened physical and mechanical properties. Polymethylmethacrylate after irradiation by shortwave ultraviolet radiation in a vacuum at normal temperature degrades and is depolymerized. Under conditions of space this effect is accelerated as a result of the temperature increase of the plastic caused by the absorption of infrared rays.

Transparent polystyrene yellows rapidly during irradiation by ultraviolet radiation.

The change in the properties of rubber mixtures depends strongly on the type of reactions flowing in them. Tensile strength and relative elongation can both increase and decrease. For instance, strength and elongation of butadiene-styrene and butadiene-acrylonitrile rubbers diminish, whereas in butyl rubber they increase. The magnitude of residual deformation of rubber-like materials during the combined effect of vacuum and temperature increases.

The Influence of Corpuscular Radiation

During irradiation in air polytetrafluoroethylene degrades very rapidly. During irradiation in the absence of oxygen or in

a poor vacuum (10^{-2} to 10^{-4} mm Hg) this polymer possesses higher radiation stability and to some measure is able to retain its initial characteristics at least in the case of very low irradiation doses. Irradiation in a high vacuum up to very low doses increases the strength of polytetrafluoroethylene. During the irradiation in a vacuum no lower than 10 mm Hg up to very significant doses degradation already flows, although to a moderate degree. The change in tensile strength and relative elongation of polytetrafluoroethylene during γ - irradiation are given in Table 36. During irradiation in air the threshold of damage for polytetrafluoroethylene comprises 1.7 Mrad, and the threshold of 25% damage - 3.4 Mrad.

Table 36. Influence of γ-irradiation on the characteristics of polytetrafluoroethylene.

Conditions of irradiation	Dose, Mrad	Relative elongation, %	Tensile strength, kgf/cm^2
Atmosphere	0	115	210
	0.1	152	140
	0.5	37	110
	1.0	21	90
	5.0	Brittle	
Vacuum (10^{-6} mm Hg)	1.0	92	175
	5.0	73	140
	51.0	38	115
	150.0	16	56

Nylon possesses very high radiation resistance to the action of corpuscular radiation. The threshold of damage was reached at a dose of 86 Mrad, and the threshold of 25% damage - at a dose of approximately 10^5 Mrad.

Polyethylene withstands irradiation up to a dose of 1000 Mrad, and the threshold of 25% damage was reached at a dose of 9300 Mrad. The radiation stability of polyethylene films does

not depend on thickness. A noticeable change in their properties occurs over the range of 440-870 Mrad. During irradiation in air polyethylene is oxidized, and therefore the final properties of the product depend on the thickness of the product. The high-density polyethylene is more susceptible to radiation damage than low-density polyethylene.

The radiation stability of polypropylene is lower than polyethylene. At an irradiation dose which corresponds to the threshold of 25% damage of polyethylene, polypropylene was completely broken. Irradiation up to a dose of 8700 Mrad converts it into a brittle material which has completely lost its elongation and barely preserved its strength.

Polycarbonates possess very high radiation stability. The irradiation dose at which brittleness is arleady so great that testing them on a dynamometer cannot be done comprises 26,000 Mrad.

The characteristics of electrical insulating materials given above give a general idea about their suitability for exploitation under the specific conditions which are characteristic for space. At the same time when selecting material for the indicated conditions it is necessary to take into account the concrete application of the space object, the duration of its stay in orbit, and the disposition of orbit relative to the Van Allen belts of the earth.

From this viewpoint there is interest in the investigations carried out by the "Bell Telephone Laboratories" [444] relative to the conditions in which a communication satellite is found. The present data show that the duration of stay of such a satellite in orbit can comprise 5-15 years [445]. The radiant flux fixed

with the help of the "Telstar 1" satellite was significantly higher than determined by Van Allen [446-448]. Since the satellite is found altogether only 20% of its total time of stay in orbit in the field of the Van Allen belts of the earth, and in the other sections of orbit the flux drops very rapidly, then the average flux on the orbit of the "Telstar 1" satellite during a period of several months comprised approximately 10^8 electrons/($cm^2 \cdot s$) at electron energies above 200 keV. During the investigation of the properties of materials an 18-year duration of operation of the satellite in orbit was assigned. Therefore the irradiation dose of electrons with a energy of 1 MeV comprised $1 \cdot 10^8$ electrons/($cm^2 \cdot s$) $\times$ 5.8×10^8 s = 5.8×10^{16} electrons/cm^2. The samples of all investigated materials before and after irradiation were subjected to physicomechanical and electrophysical tests specified by the appropriate standards.

Table 37 contains a list of tested materials and also data on the change in their physicomechanical characteristics. Some materials after irradiation were so brittle that their characteristics could not be determined.

The table shows that in the majority of samples of polyethylene tensile strength and relative elongation after irradiation were lowered. The hardness of polyethylene (3) of low density remained almost invariable, and that of the polyethylene (36) pigmented with soot increased.

Polypropylene (7) and (8) became softer by approximately 25%, but tensile strength and relative elongation were considerably decreased.

In polyamids (9)-(11) hardness and tensile strength noticeably increased, but relative elongation was almost wholly lost.

Table 37. List of the investigated materials, their characteristics and integral flux of irradiation.

Number	Material	Characteristics of material	Integral flux of irradiation 10^{15} e-electrons/cm^2	Shore hardness		Tensile strength kg/cm^2		Relative elongation, %	
				Initial	After irradiation	Initial	After irradiation	Initial	After irradiation
1	Polystyrene	General purpose	5.8	87	86	560	280	4.2	2.8
2	Polyethylene	0.95 g/cm^3, natural	5.8	67	64	210	120	665	10
3	"	0.92 g/cm^3, black, melt index 0.2	5.8	55	55	140	77	797	8
4	"	0.92 g/cm^3, natural	5.8	71	69	270	290	1365	14
5	"	0.92 g/cm^3, natural, melt index 2.0	5.8	50	70	100	70	1110	9
6	"	0.947 g/cm^3, natural	5.8	68	62	133	147	430	13
7	Polypropylene	Low density	5.8	100	74	182	7	330	43
8	"	High density	5.8	100	73	210	14	1470	59
9	Polyamide	Type 66	5.8	79	86	455	820	616	33
10	"	Type 610	5.8	77	83	442	660	100	23
11	"	Type 6	5.8	74	86	415	800	520	43
12*	Polymethyl methacrylate	Cast	1.22	-	-	-	-	-	-
13*	Acetal	Copolymer	1.22	-	-	-	-	-	-
14*	Acetal	Homopolymer	1.22	-	-	-	-	-	-
15*	Polytetrafluoroethylene	Fluorocarbon	1.22	-	-	-	-	-	-
16*	Polyfluoroethylenepropylene	Copolymer	3.67	-	-	-	-	-	-
17*	Polychlorotrifluoroethylene	Homopolymer	3.67	-	-	-	-	-	-
18*	Polyvinyl chloride	Plasticized by dioctyl phthalate	3.67	-	-	-	-	-	-
19*	Polyvinylidene chloride	Homopolymer	3.67	-	-	-	-	-	-
20	Copolymer of styrene with butadiene	With high impact strength	5.8	73	86	120	77	25	2
21*	Allyl carbonate	Cast	4.1	-	-	-	-	-	-
22*	Polyvinyl chloride	Rigid	4.1	-	-	-	-	-	-
23	Copolymer of styrene with acrylonitrile		5.8	87	87	610	400	5.5	2.9
24	Copolymer of styrene with butadiene and acrylonitrile	Natural	5.8	78	88	300	126	24	1.6

Table 37 (Cont'd).

Number	Material	Characteristics of material	Integral flux of irradiation 10^{16} electrons/cm²	Shore hardness		Tensile strength kg/cm²		Relative elongation, %	
				Initial	After irradiation	Initial	After irradiation	Initial	After irradiation
25	Copolymer of styrene with divinylbenzene	Cross-linked	5.8	86	88	525	605	6.5	6.9
26*	Cellulose acetate	Transparent with a thickness of 0.254 mm	5.8	-	-	-	-	-	-
27*	Cellulose propionate	Transparent	4.1	-	-	-	-	-	-
28*	Cellulose butyrate	"	4.1	-	-	-	-	-	-
29*	Chlorinated polyester	Natural	2.9	-	-	-	-	-	-
30*	Polycarbonate	Transparent, with a thickness of 0.381 mm	5.8	-	-	-	-	-	-
31	Polyvinyl chloride-acetate	The same	5.8	78	76	490	510	98	11
32	Polyethylene terephthlate	Light-stabilized, with a thickness of 0.127 mm	5.8	81	**	1580	**	108	**
33	Polyurethane	Elastomer	5.8	43	72	475	196	1135	13
34*	Polyvinyl fluoride	Thickness 0.102 mm	5.8	-	-	-	-	-	-
35	Polyethylene terephthalate	Usual, thickness of 0.127 mm	5.8	84	**	1570	**	100	**
36	Polyethylene	Melt index 0.2 with 2.6% soot	5.8	53	62	161	84	1125	9

*After irradiation the mechanical properties of these materials could not be determined as a result of significant degradation.

**Cannot be measured.

The characteristics of polyethylene terephthalate (32) and (35) after irradiation could not be measured.

In work [436] it has been shown that polystyrene at relatively low amounts of radiation is the most radiation resistant as compared with the other polymers. Based on the results of the investigation for polystyrene (1) hardness practically did not change but tensile strength and relative elongation were lowered by approximately 50%. The copolymer of butadiene with styrene (20) is less resistant to radiation than polystyrene. The radiation stability of the copolymer of acrylonitrile with styrene (23) is approximately the same as for polystyrene itself.

Polyurethane (33) possess low radiation stability. This elastomer becomes solid, strength with rupture diminishes, and relative elongation approaches zero.

The investigation of the electrical properties of these materials showed the following.

Only in two plastics (whereas both on the basis of styrene) dielectric permeability is not changed as a result of irradiation: in polystyrene (1) and the system styrene-divinylbenzene (25). This agrees with the results of works [12, 14, 236, 449], in which it has been established that polymers containing benzene rings, and in particular those in which this molecular grouping comprises a significant fraction of the molecule and is located in a side chain, possess high radiation stability and are subjected to the action of ionizing radiations to an insignificant degree. In the other two plastics on the basis of styrene, (20) and (24), the dielectric permeability increases by less than 1.5%. However, in the copolymer of styrene with acrylonitrile (23) the dielectric permeability at a frequency of 1 kHz increases by more than 6%. This is conditioned by the fact that the part of the molecule

containing the benzene ring it not retained and therefore the substance is more susceptible to the action of ionizing radiation.

The dielectric permeability of the hydrocarbons of a linear structure - polyethylene and polypropylene - is changed very little (less than 2%). Such small changes in the properties of aliphatic polymers were already observed earlier. Actually in work [450] when evaluating the radiation stability of polymers polyethylene is given preference over polystyrene. Although under the action of ionizing radiations the structure of a polymer and the nature of the chemical bonds between molecules is changed, on the whole compensation which conditions a small change in properties occurs.

In Fig. 29 it is shown that the dielectric permeability of polyethylene, polypropylene, and polymers on the basis of styrene both before and after irradiation remains at a sufficiently low level. A characteristic feature of polyamides (9) and resins (10) and (11) is a decrease in dielectric permeability at a frequency of 1 kHz after irradiation by electrons; at a frequency of 1 MHz this effect is manifested more weakly. In Fig. 29 the data for all materials are given only at a frequency of 1 kHz because at high frequencies the change is usually considerably less.

The dielectric permeability of polyvinyl chloride-acetate (31) after irradiation by electrons increases noticeably, probably as a result of the combined influence of breaks in chains and the appearance of the possibility of the rotation of polar groups. Undoubtedly cross-linking also occurs, but not to such a degree as to compensate for the remaining effects. Polyurethane (33) is the only material whose dielectric permeability at a frequency of 1 MHz decreases more strongly than at a frequency of 1 kHz.

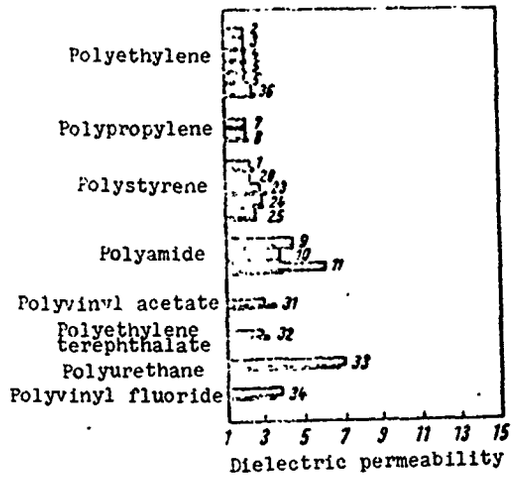


Fig. 29. The influence of irradiation by electrons on the dielectric permeability of polymers (f = 1 Khz) integral flux $5.8 \cdot 10^{16}$ electrons/cm^2 (numerals correspond to Table 37): ▭ - nonirradiated. ▬ - irradiated.

Polyurethanes have a complex molecular structure and contain atoms of nitrogen and oxygen, and also carbonyl groups in chains connected to the atoms of carbon. The cross-linking induced by irradiation can decrease polarity at a higher frequency. Polyvinyl fluoride (34) behaves in the same manner as polyurethane at a frequency of 1 kHz, however, the decrease in dielectric permeability at a frequency of 1 MHz in it is the same as a frequency of 1 kHz.

The dielectric permeability of polyethylene terephthalate (32), which contains a light stabilizer, barely changes after irradiation. Unfortunately the brittleness of this material after irradiation increases so much that it cannot be used as insulation.

All plastics are noticeably different in the original value of dielectric permeability and based on this it is possible to divide them conditionally into two basic groups: with low

dielectric permeability, which includes polyethylene, polypropylene, and polymers on the basis of styrene, and with high dielectric permeability, which includes all the remaining materials given in Fig. 29. Beyond the conventional boundary the value of dielectric permeability is taken equal to three. It is interesting that irradiation up to a high dose does not influence the relative affiliation of a material to this or that group, even if it considerably diminishes the high values of dielectric permeability of the materials of the second group (with a high ε). At the same time plastics with low dielectric permeability are most stable during irradiation.

The change in the loss factor, i.e., the product of dielectric penetrability and the dielectric power factor (Figs. 30 and 31), conditioned by irradiation, is sufficiently great and in most cases amounts to an increase in this parameter. This is especially valid for the group of the best insulating materials with small values of dielectric permeability and loss factor. The increase reaches hundreds of percents, and for polyethylene - even 2000%. An important observation, somewhat softening the influence of this undesirable trend in the change in the dielectric loss factor, consists of the fact that the majority of the materials which have a low value of dielectric loss factor in the initial state even after a significant increase in this parameter as a result of irradiation remain in the same category of good electrical insulating materials: the values of their dielectric loss factors all the same remain lower than the majority of materials with high dielectric permeability both before and after irradiation, despite the significant decrease in this parameter which is revealed for the majority of materials of the second group.

As it was noted, the most radiation resistant materials are polystyrene (1) and the styrene-divinylbenzene copolymer (25). Irradiation by electrons diminishes them even without a low loss factor at a frequency of 1 kHz and does not cause significant

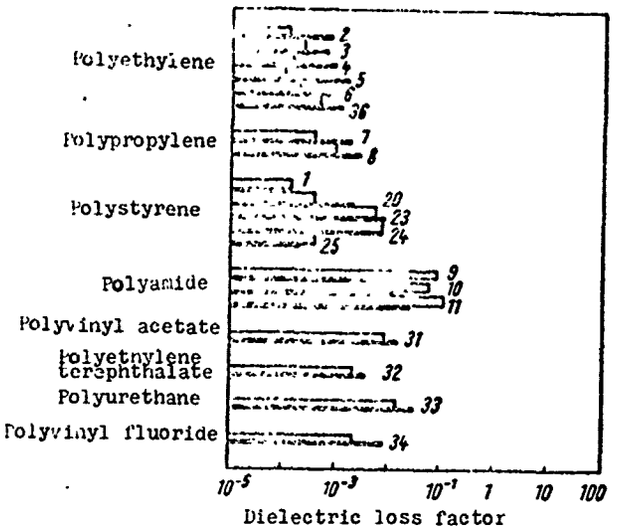
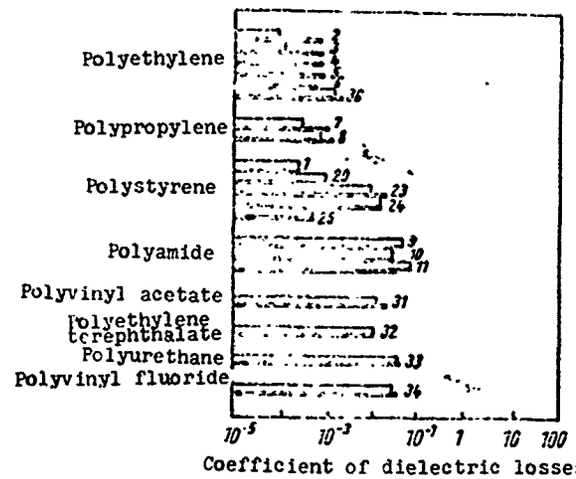


Fig. 30. The influence of irradiation by electrons on the dielectric loss factor of polymers (f = 1 kHz) integral flux $5.8 \cdot 10^{16}$ electrons/cm^2 (numerals correspond to Table 37):
□ - nonirradiated; ■ - irradiated.



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Fig. 31. The influence of irradiation by electrons on the dielectric loss factor of polymers (f = 1 MHz), integral flux $5.8 \cdot 10^{16}$ electrons/cm^2 (numerals correspond to Table 37):
□ - nonirradiated; ■ - irradiated.

changes in this parameter at a frequency of 1 MHz. In the system acrylonitrile - butadiene - styrene (24) the loss factor also diminishes slightly at a frequency of 1 kHz and is not changed at a frequency of 1 MHz, but the original value of the loss factor in it is significantly higher. In the copolymer of styrene and acrylonitrile (23), which has in the initial state a loss factor of the same order as also in a triple copolymer (24), an increase is observed in this parameter at both frequencies, whereupon more significant at a frequency of 1 MHz. The copolymer of butadiene and styrene (20), which in the initial state has a relatively low value of loss factor, displays an increase of it by more than 300% at a frequency of 1 kHz and an insignificant increase at a frequency of 1 MHz; such a behavior is apparently conditioned by the presence of butadiene.

During irradiation polymaides are considerably improved; the loss factor diminishes noticeably, but in the initial state it is so great that it is impossible to examine this material as a high-frequency dielectric.

A very important parameter is the resistance of insulation to direct current. The materials in which the greatest relative increase in the loss factor is observed, i.e., polyethylenes, reveal the greatest decrease in the resistance of insulation (Fig. 32). For instance, after irradiation by electrons the insulation resistance of polyethylene is lowered by 2-3 orders of magnitude (besides the carbon black composition). Despite the noted lowering in the magnitude of the insulation resistance of polyethylene, its value nevertheless remains significantly higher than in the majority of other plastics since the original values are so great that they frequently exceed the upper limit of measurements of the equipment utilized.

Various types of polypropylene behave differently.

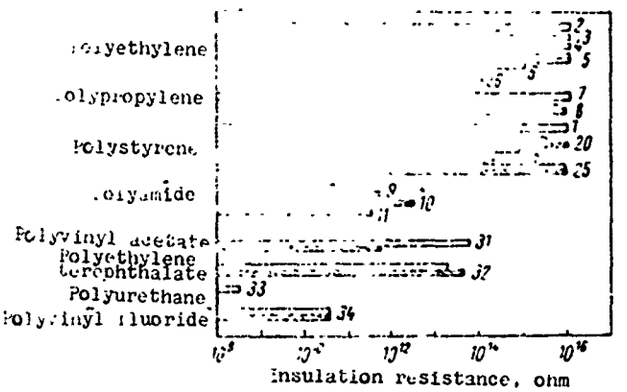


Fig. 32. The influence of irradiation by electrons on the insulation resistance of polymers to direct current, integral flux $5.8.10^{16}$ electrons/cm^2 (numerals correspond to Table 37): ▭ - nonirradiated; ▬ - irradiated.

The insulation resistance of polystyrene (1) against expectation is lowered by more than two orders, and that of the system styrene - diviylbenzene (25) is changed so little that it does not yield to measurement. In the two polymers on the basis of styrene (20) and (24) the insulation resistance increases somewhat, whereas in the copolymer of styrene with acrylonitrile (23) it is lowered by one order of magnitude.

The insulation resistance of three various polyamides which have relatively low original values of this parameter improves approximately by one order during irradiation. In the majority of the remaining materials, the insulation resistance of which in the initial state is relatively low, the changes after irradiation are small or are generally absent, with the exception of polyvinyl chloride-acetate, in which the decrease reaches approximately two orders.

If as a criterion for the evaluation of material we take the insulation resistance to direct current, then not in one

of the examined plastics is the change in this parameter as a result of irradiation so considerable that the material could not be used as electrical insulation for elements of instrumentation of a communications satellite on the condition that in initial state these materials satisfied the requirements shown for the electrotechnical and radiotechnical parts of such an application.

The measurement of the insulation resistance, which depends both on volumetric and on surface specific resistance, is a more reliable method for the evaluation of electrical insulating material than measurement of only the surface or only the volumetric specific resistance.

Summing up the results of vast experimental material it is possible to make the following conclusion.

After irradiation by electrons with an energy of 1 MeV up to an integral flux of $\sim 5.8 \cdot 10^{16}$ electrons/cm^2, i.e., about 1000 Mrad, the physical properties of acrylic, cellulose, fluorine-containing polymers, acetyl resins, and polycarbonates are so deteriorated (even at lesser doses than the indicated maximum) that neither their physicomechanical nor electrophysical characteristics could be determined. The predominant effects in materials for which it was possible to determine mechanical and electrical characteristics were the appearance of brittleness which was accompanied by a decrease in relative elongation, an increase in the loss factor, and a decrease in insulation resistance. It has been established that the most radiation resistant plastics are polymers on the basis of polyethylene and polystyrene.

On the whole the selection of material should be done on the basis of an analysis of those of its properties which have a greatest value in the given concrete case of application.

THE USE OF IONIZING RADIATIONS FOR MODIFYING THE PROPERTIES OF POLYMERIC ELECTRICAL INSULATING MATERIALS

If as a result of a reaction which flows in a polymer under the action of ionizing radiation degradation occurs, then the properties of material after irradiation are usually changed in an undesirable direction. The strength of the material during degradation is reduced as a result of the shortening of macromolecular chains.[1]

As a rule cross-linking causes favorable changes in the properties of the majority of materials, if they are irradiated up to a properly selected dose under adequate conditions. The modulus of elasticity and tensile strength increase, and the yield point also usually increases. Cross-linking conditions an improvement in the stability of a material to deformation during heating and increases resistance to the action of solvents [292]. However, along with these improvements in characteristics some undesirable effects can occur. During the cross-linking of a polymer its hardness increases and its impact strength diminishes. The plastic properties of the material are lost to a considerable degree.

There is the possibility with the help of radiation to produce a change only in the surface layer of a material. By means of irradiation it is possible to graft another polymer to

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[1]Experimental investigations showed that at a certain irradiation dose in the air the tensile strength of polytetrafluoroethylene increased, probably as a result of an increase in the degree of crystallinity [406]. However, this case of the improvement in the characteristics of material during degradation is an exception, not a rule.

the surface of the initial polymeric material. The surface treatment of a material with radiation can improve its susceptibility to painting or increase its adhesive properties.

Despite that fact that the improvements in the characteristics of plastics which are caused by their irradiation can be accompanied by some undesirable effects, there is the definite possibility of the development of processes of improvement of properties with the help of radiation exposure.

Radiation modification is a unique physicochemical method for the directed change in the properties of initial materials, whereupon the desired result is achieved in most cases without the introduction of foreign auxiliary substances into the system (vulcanizing agents, initiators or catalysts of the reaction, solidifying agents, etc.).

One of the most important goals attained with the help of radiation modification is increasing the heat resistance of polymers.

The process of increasing the heat resistance of polymers is most developed relative to polyethylene. This is conditioned basically by two reasons. In the first place this polymer is a relatively simple system in which the process of cross-linking flows with an explicit prevalence over the process of degradation. In the second place polyethylene as a result of a very favorable matching of its inherent electrophysical, physicomechanical, and technical properties, and also relatively low cost, is used widely as electrical insulation; at the same time the comparatively low heat resistance in a number of cases limits the possibilities of its use. Therefore the prospects of increasing the heat resistance of this material by means of radiation modification without a deterioration of the remaining characteristics naturally is of significant practical interest.

The possibility of increasing the heat resistance of polyethylene by means of irradiation with ionizing radiations was established long ago [451]. Along with increasing the heat resistance conditioned by the formation of a three-dimensional structure the irradiation of polyethylene adds to it a series of valuable properties, considerably expanding the adaptability of this material under specific conditions as compared with non-irradiated polyethylene. Thus, for instance, irradiated polyethylene does not flow at a temperature higher than the melting point [18] and under these conditions acquires rubber-like properties which are retained up to the temperatures of thermal decomposition (more than 300°C). With an increase of irradiation dose polyethylene loses the capacity to be dissolved in organic solvents at elevated temperatures, and its swelling diminishes [208]. Irradiation increases the resistance of polyethylene to the effect of agressive media [61, 452, 453] and reduces its tendency toward cracking under the influence of mechanical stresses and chemical reagents [454-457]. Furthermore irradiation considerably increases the electrical strength of polyethylene at elevated temperatures [335, 336, 455, 458, 459]. There are data [460] that the corona stability of irradiated polyethylene is substantially higher than nonirradiated.

The totality data given above shows that one of the most promising trends in the use of irradiated polyethylene is its use as a covering for electric wires and cables. Such an insulation ensures not only the higher heat resistance of a cable product, but also its increased reliability in operation. Ordinary polyethylene insulation even in the absence of any significant mechanical load during temporary heating up to a temperature which exceeds the melting point flows under its own weight, which gives rise to breakdown or short circuit between chains. Irradiated polyethylene insulation under analogous conditions does not flow, and under the effect of moderate

mechanical load is only somewhat strained, but is not pressed right through; the electrical strength of insulation retains a finite value and the shorting between chains is practically eliminated.

The irradiation of insulation of cable products is also useful for the refinement of some technological processes. Polyethylene irradiated up to moderate doses (20-25 Mrad) can be subjected to temporary reheating up to 150°C without substantial residual deformation. This makes it possible to accomplish, for example, the vulcanization of rubber cable sheathing with polyethylene insulation of current-conducting core wires by the usual technology accepted on equipment for uninterrupted vulcanization [461].

The methods developed for the thermal stabilization of irradiated polyethylene [221, 248-253, 333, 462], ensuring the possibility of its prolonged operation in air at elevated temperatures, make it possible to fully realize all the advantages of this material and to switch from unique uses to wide practical utilization.

It should be noted that for increasing the heat resistances of polyethylene (or another) insulation of cable products they are subjected to irradiation already in a prepared form. This means that such products are prepared by the conventional technology of cable production with the utilization of standard equipment. The difference lies in the fact that a supplementary technical operation is added - irradiation, fulfilled with the help of some source of ionizing radiation.

The technical means with the help of which irradiation is conducted at the present time have been developed sufficiently well. Since the properties of the final product depend in

practice only on the quantity of absorbed energy of radiation, and they do not depend on its form, the selection of the type, energy, and also the source of its generation is dictated by technical considerations (by the penetrating power of radiation in the irradiated material, by the possibility of obtaining a uniform absorbed dose over the whole volume of the product, by the probability of the course of undesirable nuclear reactions which are accompanied by the appearance of induced radioactivity in the irradiated material, etc.). For instance, it is evident that it is inexpedient to use accelerated heavy particles (protons, deutons, α-particles, etc.) for the irradiation of polyethylene because as a result of low penetrating power their absorption will be limited to a very fine surface layer of material[1] and the main bulk of material remains unaffected by radiation. Irradiation by neutrons usually leads to the activation of the irradiated substance, which is also undesirable because it can substantially hinder or generally make impossible any manipulation with the irradiated object for a prolonged time.

Most frequently for the radiation modification of polymers they use hard X-ray or γ-irradiation, and also electrons of sufficiently high energy. The source of high energy electrons are special electrophysical devices - accelerators of charged particles (see Chapter V). The source of hard X-radiation can be the conventional X-ray tube which is working under high voltage and also a betatron [463] or an electron accelerator of another type. As the source of γ-radiation most frequently they use radioactive isotopes which are obtained in a nuclear reactor during irradiation of appropriate targets by neutrons; the

[1] In some particular cases this method can be used precisely to cause a change only in the surface layer of a material.

most widespread isotope sources of γ-irradiation used in radiochemical processes are cobalt-60, cesium-137, and some others. The source of pure γ-irradiation can also be the radiation circuit of a nuclear reactor [464, 465], and the source of mixed β- and γ-irradiation - the spent fuel elements of a nuclear reactor [466].

The source of high energy radiation is selected on the strength of the features of the radiochemical process, the required dose rate and absorbed radiation dose, and the concrete form of the irradiated object (see Chapter V).

At the same time it is necessary to keep in mind that the entire complex of valuable properties of a polymer is attained during irradiation up to high doses; for instance, for polyethylene this dose comprises 75-100 Mrad. Since the irradiation dose is the measure of absorbed energy being spent on the realization of physical, chemical, or any other changes in a substance leading to the change in the properties of a polymer in the required direction the actuality of the question of working out a method for the achievement of the same final changes in properties with a significantly smaller irradiation dose is very obvious. Really the productivity of any radiation source (both isotope and electron accelerator) is inversely proportional to the irradiation dose required for the given radiochemical process and therefore the lowering in the irradiation dose even by several times will influence the technical-economical indices of such a process.

In this connection there is significant interest in the method for increasing the yield of the process of radiation cross-linking of some polymers (sensitization), which as was described above consists of the fact that prior to irradiation

a polyfunctional monomer is introduced into them preliminarily as an additive [264, 467, 468]. This method does not only make it possible to lower the irradiation dose for the radiation cross-linking of the polymers being "cross-linked" [272], but also makes it possible to carry out the cross-linking of "degrading" polymers. The introduction of polyfunctional monomers to polyvinyl chloride, along with the significant decrease in the irradiation dose necessary for cross-linking, eliminates [262, 263] the undesirable side process of dehydrochlorination.

The realization of the radiation modification of the polyolefin insulation of cable products, especially with the use of sensitizing additives, is a very promising procedure which has already entered the stage of industrial testing in a number of countries, including the Soviet Union.

It would seem that two alternative processes can compete with the process of radiation modification: the use of peroxide catalysts (the so-called chemical cross-linking) and the utilization of irradiation by ultraviolet light with the introduction into polyethylene of the appropriate sensitizers of photochemical absorption. However, an attentive examination of the question shows that this is not so.

Irradiation by ultraviolet light is effective only relative to very fine films or fibers.

Chemically cross-linked polyethylene contains a significant quantity of products of decay and the subsequent interaction of peroxide catalysts, which noticeably influences its dielectric characteristics. Furthermore the problem of thermal stabilization, which is quite complex for usual polyethylene, becomes almost

unsolvable for chemically cross-linked polyethylene [469]. Finally the properties of chemically cross-linked polyethylene are noticeably lower than for radiation cross-linked. This is distinctly evident from a comparison of the permissible work resources of irradiated and chemically cross-linked polyethylene [470-473]:

	Maximum temperature of prolonged exploitation °C	Emergency reheating with a duration of no more than 100 h/yr
Chemically cross-linked polyethylene	90	130
Radiation cross-linked thermal stabilized polyethylene	150	200

If chemically cross-linked polyethylene tolerates reheating up to 250°C only for 30 s, then for radiation cross-linked thermal stabilized polyethylene the permissible time of reheating is measured by tens of minutes, and at 350°C - by minutes.

Undoubtedly chemical cross-linking is accomplished more simply than radiation, and for the building of an installation in the first case less capital investments are necessary than in the second. Nevertheless the properties of products obtained in chemical and radiation cross-linking are substantially different, and each of these materials will apparently find its area of application.

In the subsequent sections the characteristics and areas of application of cable products with irradiated polyolefin insulation (including thermal stabilized) will be examined and also the fundamental types of radiation sources and the technology

of radiation modification. However, strictly the irradiation of a polymer in a product, for example a cable, for imparting to it these or other properties does not exhaust the possibility of application of the method of radiation modification.

Thus, for instance, a method has been developed [77] for the preparation of porous polyethylene by means of its irradiation in granules up to doses of 2-20 Mrad, subsequent swelling in dichlorotetrafluoroethane, and then heating and holding at 115°C in a closed vessel. By this method a uniform porous material with a density of 0.094 g/cm^2 is obtained. A variety of the indicated method is [474] the introduction of a pore former, for example dichlorotetrafluoroethane, into molten polyethylene under pressure and after irradiation up to a dose of 1-20 Mrad foaming by means of sharp lowering of external pressure. The product obtained 0.8 mm pores and a volumetric weight of 41.5 kg/m^3 - against 6 mm and 145 kg/m^3 respectively for the nonirradiated product. It is also possible [475] to use as the initial composition a solid thermoplastic polymer which in a combined state contains more than 70% monovinyl aromatic hydrocarbon and a low-boiling organic compound.

A method has been developed for obtaining a heat resistant porous polyethylene film which amounts to the following: an ordinary polyethylene film is piled in a stack and irradiated up to doses of 5-50 Mrad at a dose rate of 10^4-10^5 rad/s. In this case shrinkage of the film and adhesion occurs, which are accompanied by the formation of a large quantity of noncommunicating pores filled with air.

An original method has been proposed [409, 477] for the localization of the action of ionizing radiation on the boundary of contact of two polymeric (or others) parts by means of the introduction of boron- and lithium-containing compounds in the

surface layer of the polymer and subsequent irradiation by neutrons. This method can be used for the radiation cross-linking of pairs of heterogeneous polymeric materials or a polymer with a metal.

In certain cases for raising the molecular weight of polyethylene before its processing it is advisable to irradiate the granules up to doses of 3-10 Mrad, and then to roll at 75°C; the product obtained possesses reduced solubility and is softened at higher temperatures than initial [375]. Irradiation by γ-quanta in the presence of atmospheric oxygen over the range of 0.1-50 Mrad at -18-120°C is used for lowering the molecular weight of polyethylene [376].

The mechanical and thermal properties of mixtures of polymers can be improved by means of irradiation if compositions are prepared which consist of well mixed polymers, one of which is cross-linked and the other degrades (80 parts by weight of polyvinyl chloride and 20 parts by weight butadiene-nitrile rubber) [478].

It is also possible to vary the properties of radiation cross-linked polyethylene by irradiating compositions of it with polyisobutylene (5-95%) up to doses of 2-200 Mrad [414].

The combination of radiation (~1000-10,000 Mrad) and thermal (280°C) processing in air, and then vacuum pyrolysis at 320-820° C makes it possible to convert polyethylene into a semiconductor, the specific volumetric resistance of which can be changed from 10^{17} to 10 ohm·cm [479]. Radiation-thermal processing facilitates the formation of a developed system of a polyconjugate in irradiated polyethylene.

The cross-linkages which are formed during irradiation in a polymer fix the conformation of its macromolecules. The

deformation of an irradiated product at $T > T_{пл}$ and the subsequent sharp cooling make it possible to assign any form to it. However, repeated heating up to the same temperature restores the original forms of the product (the effect of memory). The realization of this property of irradiated polymers makes it possible to develop thermally shrunken tubes and films (see page 268).

Even such a short enumeration of the numerous available examples shows the diversity of use of the method of radiation modification of polymers and what wide possibilities their realization open in industry for purposes of both the directed change in the properties of electrical insulating materials and for the perfection and simplification of technological processes.

CHAPTER IV

CABLE PARTS WITH INSULATION MADE FROM IRRADIATED POLYOLEFINS

The development of methods of thermal stabilization of irradiated polyethylene, the accumulation of data on its efficiency at elevated temperatures in various media (air, vacuum, inert gas, water under pressure, and others) and in fields of ionizing radiations, and also the analysis of changes in strength characteristics and physicochemical properties of this material during thermal and radiation aging made it possible to use this material as thermoradiation insulation for wires and cables.

CHARACTERISTICS OF CABLE PARTS AND SOME AUXILIARY MATERIALS

Wiring leads. In the works [181, 251] detailed studies are made of the electrophysical, physicomechanical, and climatic characteristics of wiring leads with irradiated polyethylene insulation, including thermostabilized by special combined additives, which were developed by the authors.

Figure 33 shows the dependence $R_{из}$ of samples of wiring leads [copper, tin-plated, pliable cores with a section of 0.35 mm^2; insulation - polyetnylene cable brand PE-500 without additives, type II [VTU MKhP 4138-55] (ВТУ МХП 4138-55) with a radial thickness of 0.3-0.4 mm], irradiated by electrons with an energy of

3.5 MeV in air up to a dose of about 150 Mrad, on the duration of stay in various gas (vapor) media at temperatures of 200 and 300°C. The absolute values $R_{из}$ of samples of leads which were maintained in various media at a temperature of 200°C fluctuate within the limits of $(1-2)\cdot10^8$ ohm·m, which agrees well with the values obtained in work [365] during the short-term testing of wires in a Pb–Bi alloy with a uninterrupted increase in temperature. The inspection of test samples showed that after holding for 1000 hr in an oxygen-free atmosphere at 200°C the color of the insulation changed insignificantly, and at 300°C - very strongly, although losses of elasticity of insulation in both cases were not revealed.

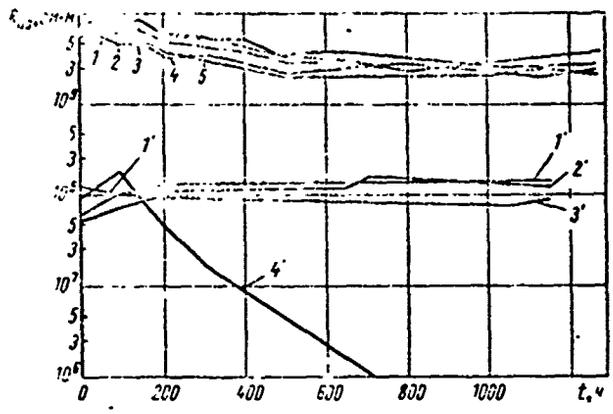


Fig. 33. Dependence of $R_{из}$ of the samples of wire with irradiated polyethylene insulation on the duration of stay in various atmospheres at 200°C (1-5) and 300°C (1'-4'): 1 - vacuum; 2 - nitrogen; 3 - helium; 4 - hydrogen; 5 - vapors of water; 1' - vacuum; 2' - nitrogen; 3' - helium; 4' - air.

Wires with irradiated insulation made from polyethylene which was thermostabilized with special additives were tested in air at temperatures of 150 and 200°C. The construction of samples differ from that described above by the fact that the section of the core comprised 0.5 mm^2 and prior to the laying on of polyethylene insulation the core was wrapped with glass fiber No. 80 in two

layers (radial thickness of winding 0.14 mm, and polyethylene 0.3 mm).

During testing the loss of elasticity of insulation, freeze resistance, insulation resistance, moisture resistance, electric strength, and radiation stability were determined.

An analysis of the results of the determination of the loss of elasticity during aging in air at a temperature of 150°C showed that a wire with insulation made from non-thermostabilized irradiated polyethylene withstands bending by a single diameter after aging for 40-50 h which a wire with insulation made from irradiated thermostabilized polyethylene withstands analogous bending after aging for 4000-5000 h. In comparative tests in the air at a temperature of 200°C it has been established that wires with insulation made from irradiated thermostabilized polyethylene tolerate bending by a single diameter after aging for 20 h against 2 h in the case of wires with non-thermostabilized irradiated polyethylene insulation.

The tests of these wires for freeze resistance (-60°C) during aging in air at 150°C showed that wires made from thermostabilized polyethylene withstand bending by a single diameter after aging for 4000-5000 h, and wire made from non-thermostabilized polyethylene - only after 200 h.

The dependence of $R_{из}$ and $U_{пр}$ of samples with insulation made of irradiated thermostabilized polyethylene on the time of stay in air at temperatures of 150 and 200°C is shown in Fig. 34. It is evident that during the initial period of testing at both temperatures the magnitude of $R_{из}$ increases somewhat, and then for a prolonged period it remains almost constant; only a weak tendency for lowering is displayed, although the absolute values remain very high. The magnitude of $U_{пр}$ is insignificantly lowered during the initial period of testing at both temperatures,

and then it is stabilized and remains practically constant for a prolonged time.

The findings confirm that wires with irradiated thermostabilized insulation retain high electrical characteristics during aging in air at elevated temperatures and the threshold of their efficiency is determined by the deterioration in physicomechanical, and not electrophysical properties of insulation.

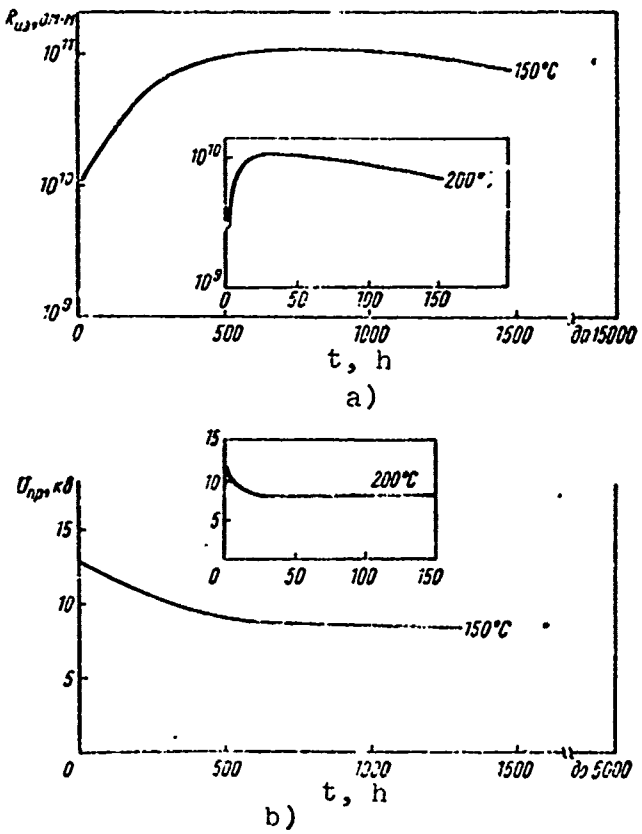


Fig. 34. Dependence of $R_{ир}$ a) and $U_{пр}$ b) wires with insulation made from irradiated thermostabilized polyethylene on the duration of aging in air.

A comparison of Figs. 33 and 34 shows that the introduction of thermostabilized additives into polyethylene places the

insulation which is being exploited in air in conditions which are close to the conditions of exploitation in an oxygen-free atmosphere. The period of time during which thermostabilized additives protect polyethylene at elevated temperatures is determined by their effectiveness and by some other properties, volatility for example.

The electrical strength of wires with irradiated polyethylene insulation both in the initial state and after aging in air for 500 h at temperatures of 120 and 150°C (it was determined by means of application of 2000 V of alternating current for 1 min on dry wires and those maintained after aging for 21 days at 40°C in an atmosphere of 98% relative humidity) remains at a sufficiently high level.

Thus the results of comprehensive tests of wires with irradiated thermostabilized polyethylene insulation showed that they possess high operational characteristics (preservation of elasticity over a wide range of temperatures, increased reliability under mechanical and thermal overloads, moisture resistance, high electrical strength, etc.); it is expedient to use them for prolonged operation in the range of temperatures of 100-200°C, i.e., namely in those cases when the use of teflon insulation (considerably more expensive and less technological) is not justified.

The use of such material in cable products attracted the attention not only of Soviet, but also of foreign scientists. Thus in work [480] the results are given from studies of the development of cross-linked thermostabilized material on the basis of irradiated polyolefins with reduced flammability, and also the characteristic of insulation for wires and cables on the basis of this material. The heat-stabilizing systems selected by the authors ensure the following permissible resources of utilization of wiring leads in air:

Temperature, °C	Length of stay, h
150	2200
175	336
200	48
250	4
300	1

In the work it was noted that by means of the preparation of special mixtures of various industrial polyolefins, the introduction of additives which lower flammability and increase the mechanical strength of this mixture and subsequent irradiation it is possible to obtain self-damping fine insulation for wiring leads, the strength of which exceeds by approximately 10 times the mechanical strength of ordinary irradiated polyethylene insulation.

Table 38. The results of comparative tests of wires with different insulation for cutting.

Load, kgf	Time, min	Deformation, mm		
		Irradiated Polyethylene	Irradiated modified composition on the basis of a mixture of polyolefins	Polytetrafluoroethylene
0.159	0	0.0762	0.0508	0.0508
0.172	0	2540	0.2032	0.1778
	5	0 94	0.2286	0.2286
	10	0.2794	0.2340	0.2286
0.286	0	Is cut through instantly.	0.2794	0.2794
	5	-	0.3302	0.3302
	10	-	0.3556	0.3556
0.399	0	-	0.3810	All cut through in from 1 to 1.75 min
	5	-	0.4318	-
0.550	10	-	0.4572	-
	0	-	All cut through in from 1 to 3 min.	-

Note. 1. The diameter of the core in all cases was 1.5 mm. 2. All the results are mean values from three measurements. 3. The thickness of insulation (radial) was 0.254 mm.

In Table 38 the results are given from comparative testing of wires with insulation from irradiated polyethylene, an irradiated modified composition on the basis of polyolefins, and polytetrafluoroethylene for cutting by a rod with a diameter of 9.127 mm and to which a specific load was applied.

From the preceding information it is evident that based on mechanical strength (resistance to cutting) irradiated modified insulation on the basis of polyolefins substantially exceeds both the ordinary irradiated polyethylene and polytetrafluoroethylene.

Coaxial Miniature Cables with Porous Insulation

Irradiated thermostabilized polyethylene recently has been used not only in the form of monolithic, but also porous insulation. This opens additional possibilities in the area of construction and production of coaxial thermoresistant cables of reduced weight and dimensions. The question of the use of porous irradiated polyethylene in coaxial lightened miniature wires and cables is examined in detail in work [481].

Up to recently only polyethylene and polytetrafluoroethylene were used as insulation for coaxial cables. However, for the achievement of the best characteristics and for expanding the field of application they began to use irradiated porous polyolefins in cables of this type.

Irradiation, as already mentioned above, increases the heat resistance of material, reduced its tendency toward cracking under stress, and eliminates cold flowing as a result of the formation of a steric network.

The preparation of porous polyethylene insulation by means of the addition of a suitable foaming agent to the initial material

has been going on for several years. However, a deficiency of such a porous material is its relatively low mechanical strength, which substantially limits its area of application. If as the initial material an appropriate thermostabilized composition on the basis of polyolefins with the addition of a foaming agent is used and the fabricated cable product is exposed to irradiation, then for porous insulation it is possible to attain the same strength which is possessed by monolithic polyethylene insulation.

The dielectric permeability of irradiated porous polyolefin insulation can be lowered to 1.5, and this already considerably improves the electrical characteristics of the cable as compared with a cable which has monolithic insulation made from the same polyolefin. The steric network formed during the irradiation of porous polyolefin conditions form stability and strength at increased temperatures. As a result during soldering of the cable core the insulation material is not deformed as a result of overheating (this has specific value when soldering has to be done in a limited space and contact between the insulation and the heated soldering iron is unavoidable).

Coaxial cables with porous irradiated thermostabilized insulation on the basis of polyolefins can be used for a long time (up to 10,000 h) at a temperature of 135°C and for a short time (up to 1 h) at a temperature of 250°C.

The irradiated protective covering superimposed on cables by the method of extrusion possess the same heat resistance as the insulation itself. The compositions used for the preparation of protective coverings possess strength, chemical stability, low specific weight, and do not support burning. The specific weight of coverings for irradiated polyolefins comprises ~1.2 g/cm^3 against a value of 2.2 g/cm^3 which is characteristic for other thermoresistant materials used for this purpose (polytetrafluoroethylene, a fluorinated copolymer of ethylene and propylene).

In cases when the economy of weight and space occupied are of special importance a braid which consists of very fine copper silver-plated flattened wire is used as the external conductor. Here the weight of the screen is reduced by more than two times, and the thickness by 2/3 as compared with a braid made from circular wire.

Today series of cables are being produced which have insulation made from irradiated polyolefin, which is the analog of miniature coaxial cables of the RG type

One of the most important problems when using miniature cables of the RG type is the break of the center conductors, the diameter of which in the majority of constructions comprises 0.25 mm. By means of utilization of irradiated porous polyolefin as insulation (ε = 1.5 against 2.05 for polytetrafluoroethylene) it is possible to preserve unchanged resistance and the outside diameter of a cable on insulation and simultaneously to almost double the section of the center conductor as compared with that used in a cable which has insulation made out of polytetrafluoroethylene. Simultaneously there is a decrease in the total damping of the cable (approximately by 20%).

At assigned wave resistance a decrease ε of insulation gives rise to a decrease in the capacity of the cable, which also produces perceptible advantages.

When using an irradiated porous dielectric it is possible, if this is necessary, to reduce the dimensions of cable while leaving the dimensions of the internal conductor unchanged. Below a comparison is given of the characteristics of RG-195 A/V cable and irradiated cable with exactly the same center conductor:

Structural element	RG-195 A/V cable		Irradiated cable	
	Material	Diameter, mm	Material	Diameter, mm
Conductor	Wire with a diameter of 0.25	0.25	Wire with a diameter 0.25	0.25
Insulation	Polytetrafluoroethylene	2.5	Irradiated porous polyolefin	2.0
Screen	Wire with a diameter of of 0.19 mm	0.07	Wire with a diameter of 0.19 mm	2.46
Covering	Polytetrafluoroethylene	3.94	Irradiated porous polyolefin	3.05

Thus the diameter of the cable is reduced by 22%, and the cross-sectional area occupied by it - by 40%.

Along with the decrease in dimensions by means of using irradiated porous and monolithic polyolefins it is possible to attain a noticeable lowering in the weight of cables. Actually the specific weight of irradiated porous dielectrics on the basis of polyolefins comprises about 0.5 g/cm^3, and irradiated protective covering of monolithic polyethylene - about 1.2 g/cm^3. These numerals can be compared with the specific weight of 2.2 g/cm^3 - a typical value for fluorinated hydrocarbons. A reduction in the specific weight of insulation material in conjunction with decrease in overall dimensions makes it possible to lower the total weight of miniature cables by 2/3 as compared with ordinary cables with analogous parameters. If for a comparison, just as earlier, we select the RG-195 A/V cable, then the following results are obtained:

Characteristics	RG-195 A/V Cable	Cable with irradiated polyethylene	
		I	II
Diameter of conductor, mm	0.25	0.25	0.25
Z, Ω m	95	95	95
Diameter of cable, mm	3.8	3.05	3.8
Weight, kg/km	7.64	2.64	4.44

In the first example (I) the central conductor has the same dimensions, therefore the outside diameter of the cable is reduced. In the second example (II) outside diameter has been maintained constant, and this made it possible to double the section of the center conductor. The total weight in this case is reduced by 66 and 43% respectively.

Thus the major advantages connected with the use of irradiated porous and monolithic dielectrics on the basis of polyolefins are reduced to the achievement of a high strength: weight ratio and the possibility to produce light thermoresistant pliable insulation coverings.

In recent years many new areas of application of coaxial cables have appeared [482], whereas under conditions when the influence of ionizing radiations is one of the fundamental factors which characterize the influence of the environment (nuclear reactors, space vehicles, etc.). Cables with insulation on the basis of irradiated thermostabilized polyclefins possess a radiation stability 100-1000 times greater than those with conventional insulation. In the absence of bending while in use (fixed

assembly) the tolerance dose of irradiation comprises 5000 Mrad, which corresponds approximately to a 10-year stay at the site of the greatest concentration of charged particles in the Van Allen belts of the earth.

Cables and Wires for the Wiring System of Space Vehicles

In a number of works, for example [483], it has been shown that cable products with modified insulation on the basis of the irradiated polyolefins containing various additives are most preferable for utilization in the electrical wiring system of man-made earth satellites and spacecrafts of various designation.

Thus a material has been proposed under the trade name of "Novaten" which represents a composition consisting of the follwoing components: 1) strictly polyolefins; 2) a system which reduces a capacity for flare up; 3) antioxidants which protect the polymer system at elevated temperatures in the air; 4) antirads, i.e., substances which protect polyolefins from the effect of ionizing radiations. After fabrication of the cable product it is irradiated.

Table 39 gives data which illustrated the weight characteristics of cable products of identical construction, but with insulation made from polytetrafluoroethylene and "Novaten."

In Table 40 the basic properties of "Novaten" and standard irradiated insulation on the basis of modified polyolefins are compared.

It is evident that the basic properties of "Novaten" differ little from the properties of standard irradiated insulation on the basis of polyolefins; at the same time the use of "Novaten" as an insulation gives an explicit gain in weight as compared with the use of polytetrafluoroethylene.

Table 39. Comparison of the properties of cable products with insulation made from "Novaten" and polytetrafluoroethylene.

Product	Diameter, mm	Weight, kg/km		Relative weighting when using polytetrafluoroethylene, %.
		"Novaten"	Polytetrafluoroethylene	
Wiring lead	0.254	0.910	1.31	44
Wiring lead	0.404	1.720	2.23	30
Wiring lead	0.645	4.326	5.06	18
Single-core shielded cable in covering (10.38 mm)	0.645	7.887	10.12	28
Two-core shielded cable in covering (0.38 mm)	0.645	20.834	23.8	19
Three-core shielded cable in covering (0.38 mm)	0.645	26.387	32.7	18
Coaxial cable RG-195 A/V	0.254/0.364	16.37	29.7	78

Table 40. Comparison of the properties of "Novaten" with standard irradiated insulation on the basis of modified polyolefins.

Properties	"Novaten"	Standard insulation
Specific weight, g/cm^3	1.18	1.15
Tensile strength, kgf/cm^2	210	210
Relative elongation, %	150	120
Freeze resistance, °C	-55	-55
Dielectric strength, kV/mm	36	32
Dielectric permeability	2.5	2.5
Volumetric specific resistance, MΩ·cm	30,000	30,000
Permissible temperature of prolonged utilization in air, °C	125	135
Permissible temperature of four hour stay in air, °C	225	225
Inflammability	Self-Damping	

Thus the use of cables with insulation made from "Noveten" makes it possible not only to substantially reduce the weight and dimensions of the airborne cable system, but also to reduce gas evolution in a vacuum, and also to practically completely eliminate the corrosion of airborne equipment (proceeding when using fluoropolymeric wire and cables coverings) with a simultaneous increase in the radiation stability of the system.

The use of irradiated polymers in the production of wires and cables is covered in a significant number of works. Irradiated polyethylene is used as an insulation both in the form of film and tapes (low-voltage power cables, aerial sound cables, aerial distribution cables, control cables, winding wires for immersion electric motors, etc.) and in the form of monolithic insulation applied by the method of extrusion [484]. The addition of active fillers and substances which decrease inflammability into polyetnylene made it possible to develop wiring leads and special-purpose cables for use under particularly harsh operating conditions, mainly in aviation and missile technology [480].

The possibilities of the application of irradiated polyethylene as electrical insulating material are also covered in works [249, 251, 296, 329, 485].

There are reports [486] that irradiated polyvinyl chloride can be used for wire insulation. As a result of the irradiation of this polymer in the presence of special additives (cross-linking agent, stabilizer, filler, etc.) heat resistance improved (it was not softened up to 300°C), solubility was lowered, and electrical properties were raised (the insulation resistance was 10 times higher than in standard polyvinyl chloride).

The irradiation of cable products with polyolefin insulation precludes cracking under stress conditions under the action of surface-active substances [484, 487].

Cables for Geophysical Prospecting
(Coring)

In recent years there has been a considerable increase in the number of deep and ultradeep oil wells with a high temperature on the face end. Many new sites are distinguished by the great depth of occurrence of productive strata (4.0-7.5 km) at high geothermal gradients.

For conducting geophysical operations in hot wells it is necessary to have coring cables with insulation ensuring $R_{из} \geq 15$ MΩ·km at operating temperatures of 150-200°C and pressures up to 100 kgf/cm^2 in drilling mud.

Irradiated polyethylene was tested [344] as one of the variants of insulation for a coring cable for industrial coring investigation in ultradeep wells. The cables had the following construction: on a two-layer steel-copper core polyethylene insulation was applied. The insulated core was irradiated with γ-quanta of Co^{60} in argon up to a dose of 140 Mrad. On the irradiated core a braid made from cotton thread was applied, and then a two-layered jacket (protection from mechanical damages and the load-bearing element). The structural length of the experimental cable comprised 7500 m.

The tests of the coring cable with insulation made from irradiated polyethylene in wells with extreme temperatures in the face layer of 150°C and pressure of drilling mud ≈800 kgf/cm^2 revealed its good operating characteristics: a maximum lowering in insulation resistance from 100 MΩ·km on the surface to 20 MΩ·km (maximum immersion in well) in the absence of mechanical deformations of insulation, and also the complete restoration of electrophysical characteristics of the insulation upon lifting the cable to the surface. A satisfactory stability of characteristics of the cable after a "run" of more than 1250 km was revealed.

In Table 41 the change is shown in the insulation resistance of cable during a double cycle of lowering and raising.

Table 41. The change in the insulation resistance of a coring cable during a double lowering into a well and lifting out.

Depth, m	Insulation resistance, MΩ			
	First cycle		Second cycle	
	Lowering	Raising	Lowering	Raising
0	—	—	—	—
500	500	—	—	500
1000	200	—	—	500
1500	200	—	—	500
2000	200	—	—	500
2500	200	—	—	500
3000	150	100	100	200
3200	—	—	—	100
3250	—	—	—	70
3500	50	40	50	50
3670	—	—	30	30
3700	25	25	—	—

The data obtained under operating conditions in conjunction with the results of laboratory investigations confirmed that insulation on the basis of irradiated polyethylene is efficient under conditions of the simultaneous influence of temperatures of 120-180°C and pressures of drilling mud greater than 1000 kgf/cm^2.

Thermosetting Film and Tube

It should be noted that the raising of the reliability and heat resistance of insulation of cable products made from polyolefins by means of their irradiation by ionizing radiation does not exhaust those promising directions which are opened to cable technology with the realization of the methods of radiation modification of polymeric materials.

For instance, the use of thermosetting insulation tubes made from irradiated polyethylene and other polymers substantially simplifies the problem of the insulation of joints (splices) of

cores with polyethylene insulation, the insulation of points of soldering of the wiring leads and output ends of electric machines and apparatuses, and also the banding of plaits of conductors; for this purpose it is possible to use a film (tape). Insulation by such a method ensures not only good electrical insulation, but also the high moisture resistance of the joints.

As the basis for the noted method the so-called memory "effect" of the irradiated polymer has been laid down [430]. The macromolecular chains of polyethylene (typical representative of polyolefins) have been arranged partially ordered and partially chaotically. Crystallites are formed in those sections where there is ordering in the disposition of macromolecular chains at distances commensurable with molecular (Fig. 35a). If polyethylene is influenced by high-energy ionizing radiation, chemical changes occur in it: the cross-linking of macromolecules into a solid steric network. Figure 35b shows the molecular structure of such a system after irradiation: the heavy lines depict the cross-linkages formed during irradiation.

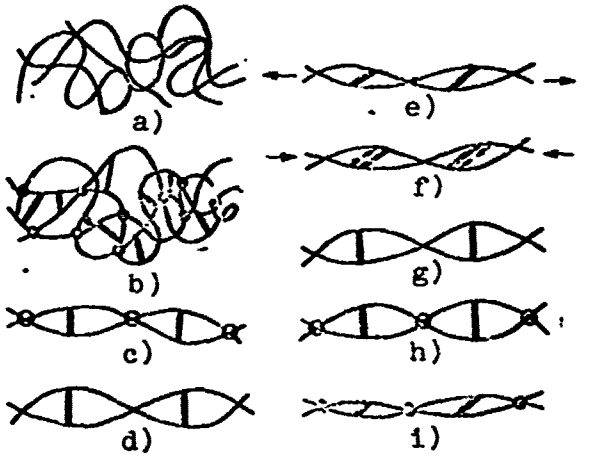


Fig. 35. The influence of crystallinity and cross-linkages on the mechanical properties of polymers.

The properties of irradiated polyethylene at temperatures lower than of the range of melting of a crystallite are determined mainly by the degree of crystallinity, the length, and the branching of molecules. These factors can be regulated to a certain degree during the preparation of the initial material. When radiation cross-linked polyethylene is heated to a temperature which exceeds the melting point of crystallites the material acquires the properties of an elastic gel, i.e., is transformed into a rubber-like state. A small force can cause deformation. However, with the removal of the applied force the material immediately acquires the original form and dimensions. In Fig. 35i the molecular structure and elastic properties of the cross-linked polymer are shown.

At room temperature cross-linked polyethylene (as also standard) possesses a high degree of crystallinity; this is shown in Fig. 35c in an example of two macromolecules. The strength of the material at room temperature is determined precisely by crystal structure. However, with an increase in temperature the crystals are melted while the cross-linkages formed during cross-linking remain (Fig. 35d).

If to the cross-linked polyethylene which has a steric structure a certain tension is applied, then the material is elastically deformed as shown in Fig. 35e. The greater the tension the more strongly the material strives to contract since the cross-linkages play the role of elastic elements which contract the macromolecules. Regardless of how long the applied force acts the molecules resist stretching with a constant force, equal to the strain applied but directed oppositely. If the effect of strain is terminated then the molecules will be almost instantly returned to their initial configuration (Fig. 35f, g).

If in this position the material is cooled then the crystal structure will again be restored (Fig. 35h). If the material is cooled during the period when stress is applied to it, then the crystal structure will fix the molecules of polymer in the stretched state as is shown in Fig. 35i.

The removal of stress at this point does not restore the initial configuration of macromolecules, since the interaction force between macromolecules in the crystallite is sufficiently great and cross-linkages will be found in a stressed state. However, if again after this the material is heated to a temperature which exceeds the melting temperature of crystallites, then the strained cross-linkages relax and the original configuration of macromolecular chains will be restored (the "memory"!).

This property is used both in films [480] and in tubes[488].

Below comparative data are given on the typical physico-mechanical properties of an irradiated multipurpose polyethylene and one that is preliminarily oriented.

	t, °C	Multipurpose	Preliminarily oriented
Thickness, mm		0.125	0.1
Yield point, kgf/cm^2	23°	94.5-129.5	More than 140
	80°	3.15-42.0	More than 85
	120°	7-14	
Relative elongation, %	23°	300-500	More than 200
	80°	300-500	The same
	120°	200-600	The same
Tensile strength, kgf/cm^2	23°	133-175	More than 210
	80°	52.5-63.0	More than 84
	120°	7-14	More than 10.5

It is evident that the oriented irradiated polyethylene possesses greater shrinkage and higher strength.

In the case of wrapping the splicing site of a core cable with an irradiated oriented film and its heating up to a temperature of 110°C the film will set and will press the cable tightly; reheating to a temperature of 135-150°C will cause the adhesion of individual layers of the film between one another and will ensure a tight hermetically sealed insulation, impermeable for water, dust, and chemical reagents. Tubes which have been irradiated and then inflated at elevated temperatures and quenched behave in the same manner; during reheating they set up to the original size and squeeze the joint tightly.

Such thermosetting tubes are produced by a number of foreign firms under various names (Termoroy, Shprinfleks, Koroplast, etc.) [transliterated from cyrillic]. Their nomenclature is sufficiently great (nominal diameter in a set state 0.6-100 mm) [489].

THE RADIATION STABILITY OF CABLE PRODUCTS

In the preceding sections it was shown that the permissible duration of exploitation of cable products in the zone of action of ionizing radiations, independent of the form of radiation, is determined in the first place by the peculiarities of the electrical insulating material used.

A detailed examination of data on the radiation stability of polymeric materials makes it possible to select correctly the covering of one or another class for the prolonged use of the cable product under conditions of radiation exposure.

Despite the fact that with every year the quantity of works dealing with the investigation of the radiation stability of electrical insulating materials is increasing all the more, information about the behavior of cable products under conditions of different forms of radiation remains limited. Such a

circumstance is apparently connected with the known difficulty of conducting such investigations and with conjuncture considerations.

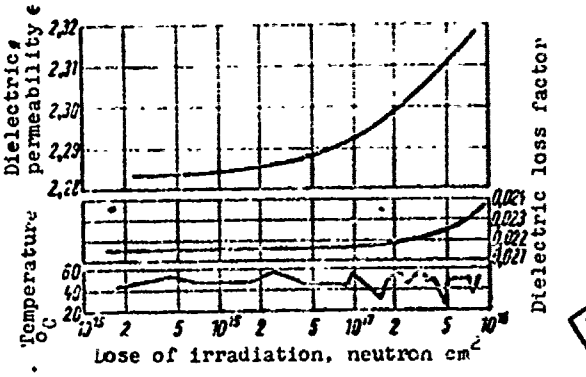
The behavior of some cable products in fields of ionizing radiations are examined below.

For evaluating the influence of radiations on the electrical parameters of radio-frequency cables over a wide range of frequencies a series of experiments have been conducted [490]. The samples of cables were placed directly into the channel of a nuclear reactor and their characteristics measured by the resonance method. Since the indicated method at frequencies above 10^3 MHz relative to samples in the form of cables is technically impracticable, the measurement of the parameters in the ultrahigh frequency range was conducted on samples of the materials entering into the composition of the cable. The irradiation of such samples in reactor is conducted in hermetically sealed aluminum containers; a series of experiments on the irradiation of materials was accomplished on a γ-source of Co^{60}.

Figure 36 shows the dependence of dielectric permeability and dielectric loss factor of irradiated polyethylene insulation of coaxial cable with a length of 12 m on the integrated flux of irradiation by rapid neturons. In this the temperature change in the reactor channel during the experiment is shown. After the cable has been in the reactor 800 h the dielectric loss factor of insulation increased by approximately 9%, and dielectric permeability changed by 4%. During this experiment it was attempted to determine the influence of breaks on the change in the indicated parameters of the cable. It was established that in this case the dielectric loss factor is not changed, but dielectric permeability increases somewhat. This is apparently connected with the temperature change of the environment.

For a comparison Fig. 37 gives an analogous dependence for a cable with a length of 12 m made from polytetrafluoroethylene

(Teflon). The increase of dielectric permeability after 600 h of irradiation did not exceed 3%. The dielectric loss factor did not change within the limits of error of measurement.



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Fig. 36. The dependence of dielectric permeability and dielectric loss factor of polyethylene insulation of a coaxial cable on the integral flux of irradiation by rapid neutrons.

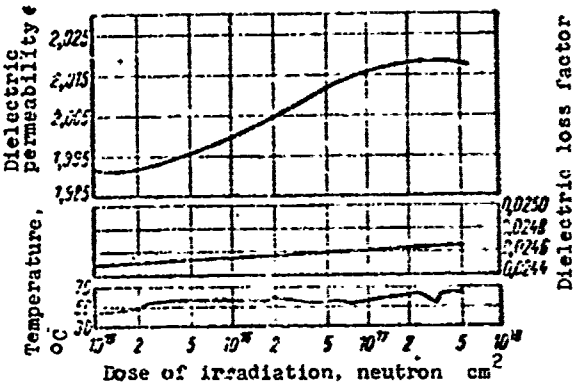


Fig. 37. The dependence of dielectric permeability and dielectric loss factor of polytetrafluoroethylene insulation of a coafial cable on the integral flux of irradiation by rapid neturons.

Figure 38 shows the dependence of the dielectric loss factor on the integral flux of neutrons for polystyrene, irradiated polyethylene, and polytetrafluoroethylene (Teflon) at frequencies of 1×10^3, 3×10^3, and 8.5×10^3 MHz. During the irradiation of polystyrene by rapid neutrons up to 10^{18} neutron/cm^2 no changes were revealed in the dielectric loss factor within the limits of measuring error. The most significant change in characteristics is noted in polytetrafluoroethylene, especially at frequencies of 1×10^3 and 3×10^3 MHz. At a dose of 1.3×10^{18} neutron/cm^2 the dielectric loss factor exceeds by five times the initial value. The dielectric loss factor of irradiated polyethylene at these same frequencies and an irradiation dose of 5×10^{18} neutron/cm^2 approximately doubles; at a frequency of 8.5×10^3 MHz changes are not detected. Since irradiation in the reactor was conducted in air a certain increase in the dielectric loss factor can be connected with radiation oxidation. It is possible that during the transition into the range of lower frequencies change in the dielectric loss factor will be expressed more sharply. The analogous dependences, obtained during the irradiation of samples on a γ-source of Co^{60}, are shown in Fig. 39. In this case, as also during irradiation in a reactor by rapid neturons, in polystyrene no substantial change is noted in the dielectric loss factor -- in contrast to polytetrafluoroethylene and irradiated polyethylene.[1] At an integral flux of 7.5×10^8 rads the dielectric loss factor for polyethylene at frequencies of $0.8 \cdot 10^3$, $1 \cdot 10^3$, and $3 \cdot 10^3$ MHz is approximately identical in absolute value, however, the nature of change during irradiation up to this integral flux is somewhat different, whereupon at the lowest frequency ($0.8 \cdot 10^3$ MHz) this dependence traverses the maximum. The increase in the dielectric loss factor of polytetrafluoroethylene up to doses on the order of $2 \cdot 10^8$ rads is insignificant, however, already at doses of $5 \cdot 10$ rads it

[1]Radiation oxidation during the irradiation on a γ-source naturally should be expressed to even a greater degree than during irradiation in a reactor, due to the considerably lower dose rate.

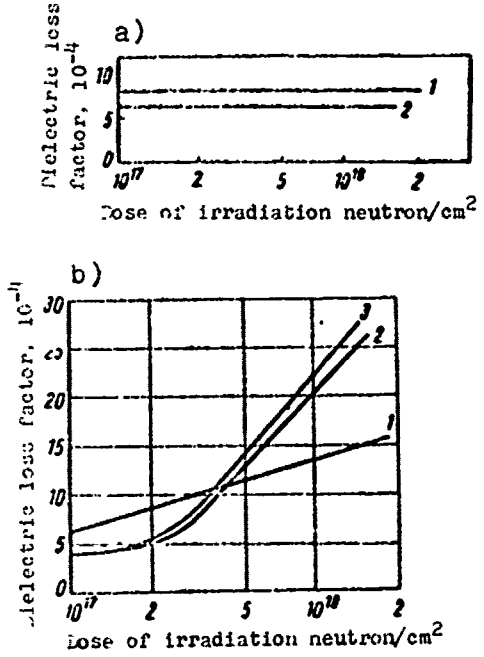


Fig. 38. The dependence of the dielectric loss factor on the integral flux of irradiation by rapid neutrons for: polystyrene a); polyethylene b); polytetrafluoroethylene c); 1 - $8.5 \cdot 10^3$ MHz; 2 - $3 \cdot 10^3$ MHz; 3 - $1 \cdot 10^3$ MHz.

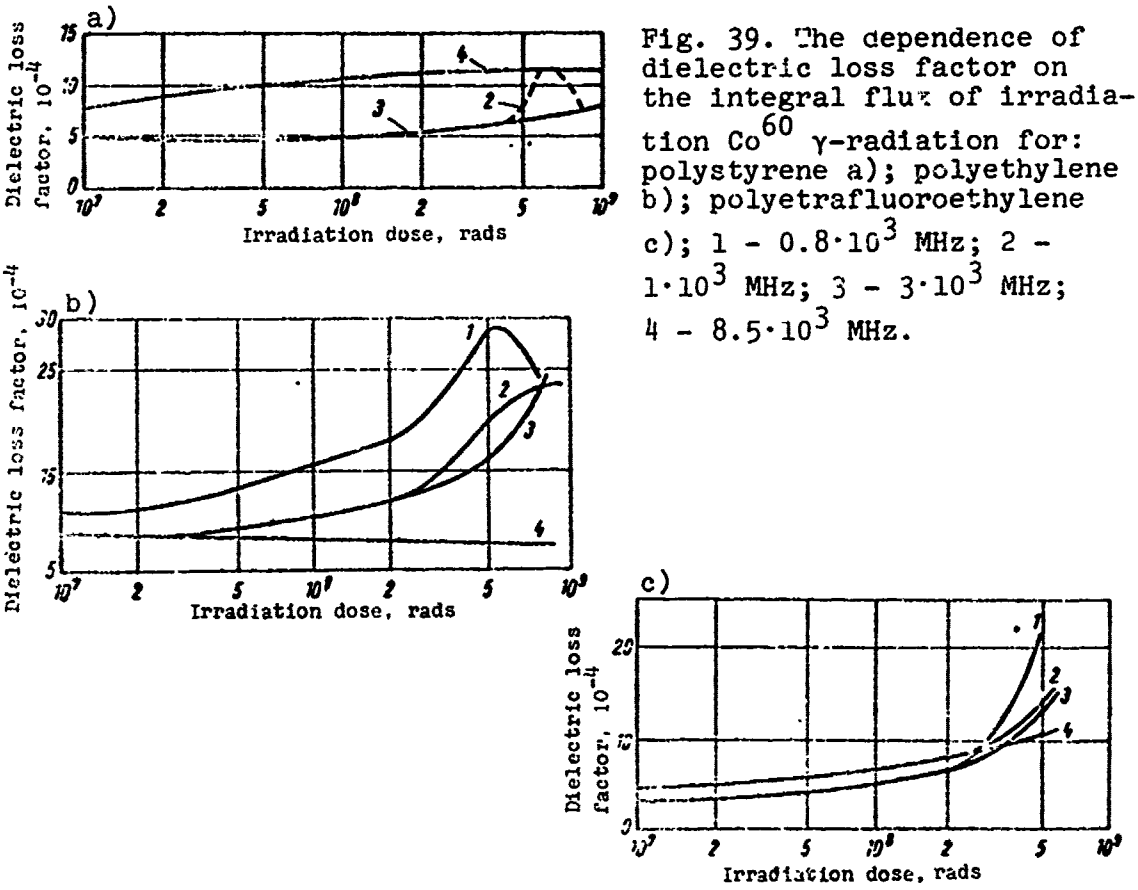


Fig. 39. The dependence of dielectric loss factor on the integral flux of irradiation Co^{60} γ-radiation for: polystyrene a); polyethylene b); polyetrafluoroethylene c); 1 - $0.8 \cdot 10^3$ MHz; 2 - $1 \cdot 10^3$ MHz; 3 - $3 \cdot 10^3$ MHz; 4 - $8.5 \cdot 10^3$ MHz.

exceeds by two-four the initial values. The greatest increase is noted a frequency of $3 \cdot 10^3$ MHz, the least - at a frequency of $0.8 \cdot 10^3$ MHz; this dependence can pass through the maximum.

Figure 40 shows the dependence of the relationship of magnitudes of dielectric loss factors of irradiated and non-irradiated samples on frequency for polyethylene and polytetrafluoroethylene, irradiated in a reactor and on a γ-source. It is evident that at a frequency less than 40 MHz the values of the dielectric loss factors of irradiated and nonirradiated materials are practically the same; over the range of frequencies of 50 to 10,000 MHz this dependence for both materials traverses the maximum, whereupon for polytetrafluoroethylene the relative increase reaches seven, whereas for polyethylene it is approximately three. It should be noted that the maximum for both materials lies in the range of 1000-3000 MHz. The data obtained for neutron and γ-radiation coincide adequately.

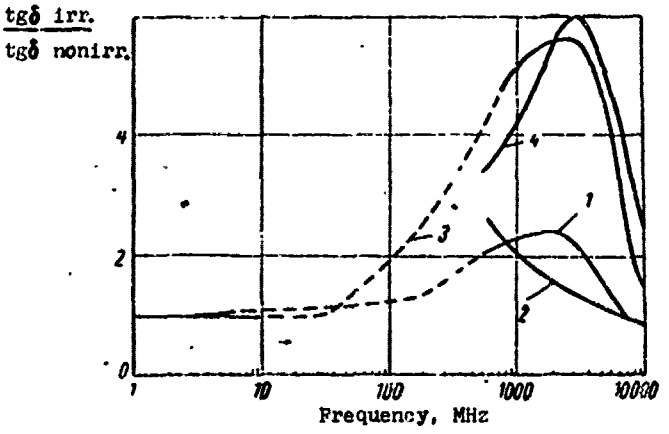


Fig. 40. The dependence of the relationship of the magnitude of dielectric loss factors on frequency: 1 - polyethylene, irradiation in a reactor up to $5 \cdot 10^{18}$ neutron/cm^2; 2 - polyethylene, irradiation on a γ-source up to $5 \cdot 10^8$ rads; 3 - polyetrafluoroethylene, irradiation in a reactor up to $1.3 \cdot 10^{18}$ neutron/cm^2; 4 - the same, irradiation on a γ-source up to $5 \cdot 10^8$ rads.

Cables with insulation made from irradiated thermostabilized polyethylene (wiring leads) were tested for radiation stability in the channel of a nuclear reactor at thermal neutron fluxes of 5×10^{12} neutron/($cm^2 \cdot s$) and accompanying γ-radiation with an intensity of 50 Mrad/h up to an integral flux of 1.15×10^{18} neutron/cm^2 in an atmosphere of argon at a temperature of 160°C. During testing under operating conditions insulation resistance was determined, its electrical strength was checked with a voltage of 500 V direct current. At the indicated integral flux of irradiation by mixed (n, γ)-flux (physical dose comprised 3500 Mrad) a noticeable deterioration in the electrical characteristics of cables was not revealed.

The dependence of $R_{из}$ of a wire with polyethylene insulation and sublayer of fiberglass on integral neutron dose at room temperature is shown in Fig. 41. It is evident that the insulation resistance decreases linearly with an increase in the integral flux of irradiation, whereupon for the values obtained in the absence of flow (measurements fulfilled right after the trip-out of power) an analogous regularity is observed; after holding for an hour the insulation resistance is restored to the initial (prior to irradiation) values.

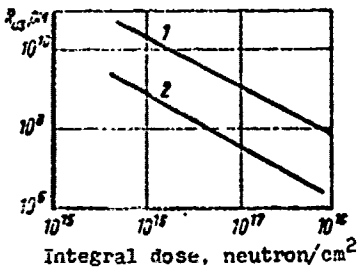


Fig. 41. Dependence of $R_{из}$ of a shielded wire with insulation made from polyethylene and sublayer made from fiberglass on integral flux: 1 - at zero power; 2 - during irradiation.

Figure 42 shows the dependence of $R_{из}$ of wires with insulation made from radiation cross-linked polyethylene on the intensity of neutron flux. The results obtained in a semilogarithmic scale set satisfactorily on a straight line, whereupon the exponent in

the index is equal to 0.75, which coincides well with the theoretical value of this coefficient for polyethylene [365].

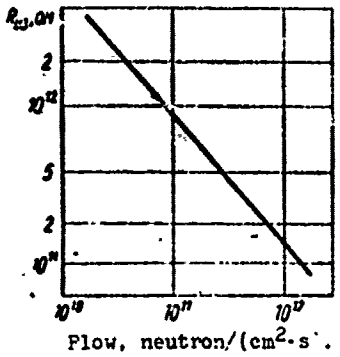


Fig. 42. Dependence of $R_{из}$ of a shielded wire with insulation made from radiation cross-linked polyethylene on the intensity of neutron flux.

For these samples of wires the dependence of insulation resistance on integral flux, obtained at a temperature of 160°C, is shown in Fig. 43. Up to the doses of a order of $3 \cdot 10^{17}$ neutron/cm^2 $R_{из}$ increases somewhat and then is stabilized and remains at the same level up to doses of $2 \cdot 10^{18}$ neutron/cm^2.

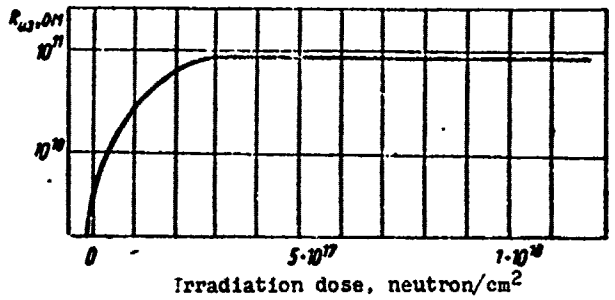


Fig. 43. Dependence of $R_{из}$ of shielded wire with insulation made from radiation cross-linked polyethylene on integral flux.

The data given above show that cable products with irradiated polyethylene insulation possess a high radiation stability. When irradiated thermostabilized polyethylene, containing some antirad additives along with antixoidants, is used in cables, during prolonged irradiating at elevated temperatures in air not only are the electrical properties of the insulation retained, but also

its elasticity. High radiation stability in conjunction with high heat resistance at high electrophysical characteristics make it possible to consider this material as one of the most promising for utilization as a covering for wires and control cables and protection of installations, the operation of which is connected with the presence of the nuclear (ionizing) radiations of high intensity.

CHAPTER V

SOURCES OF IONIZING RADIATIONS AND THE TECHNOLOGY OF RADIATION MODIFICATION

SOURCES OF IONIZING RADIATIONS

The sources of ionizing radiations based on principle of generation are subdivided into three groups: 1) nuclear reactors; 2) isotope sources; 3) charged-particle accelerators.

For the radiation modification of polymers it is possible to use any sources of the ionizing radiations, however, the technical expediency and the economic effectiveness of the use of one or another radiation source are determined by the peculiarities of the particular radiochemical process.

Below the operating principles and basic parameters of various sources of the ionizing radiations are presented, and also the principles, on the basis of which the source for a specific radiation process is selected are given.

Nuclear Reactors

The description of the principles of calculation, construction of nuclear reactors, and also exploitation are covered in a large number of works [491-498].

A nuclear reactor is an installation in which under specific controlled conditions a chain (self-sustaining) fission reaction of the nuclei of heavy elements occurs, for example U^{235}, Pu^{239}, Th^{233}, and others. The process of fission leads to the formation of fission products which as a rule are radioactive and transform into a stable state by means of a series of successive radioactive transformations with the emission of β- and γ-radiation; these processes are also accompanied by the emission of neutrons and γ-quanta. Below is given the fission reaction of the U^{235} nucleus leading to the formation of fission products which, having undergone a chain of successive transformations, are converted into stable isotopes:

$$_{92}U^{235}(n, 2n)_{40}Zr^{97} + {}_{52}Te^{137}$$

$$_{40}Zr^{97} \xrightarrow{\beta} {}_{41}Nb^{97}$$

$$_{41}Nb^{97} \xrightarrow{\beta} {}_{42}Mo^{97}$$

$$_{52}Te^{137} \xrightarrow{\beta} {}_{53}I^{137}$$

$$_{53}I^{137} \xrightarrow{\beta} {}_{54}Xe^{137}$$

$$_{54}Xe^{137} \xrightarrow{\beta} {}_{55}Cs^{137}$$

$$_{55}Cs^{137} \xrightarrow{\beta} {}_{56}Ba^{137}$$

The sum of the masses of end products of fission is less than the mass of the initial nucleus by a magnitude equivalent to the binding energy (the mass defect). Therefore the process of fission is accompanied by the generation of energy on an order of 195 MeV for every act of fission. About 95% of this energy is freed instantly, and the remainder liberated during the radioactive decay of the fission products. Neutrons and γ-quanta, emitted by the initial nucleus, are called instantaneous, and those emitted by the fission products - delayed.

The fission energy, MeV, is distributed in the following manner [493]:

Fission neutrons	6
Fission products	182
Instantaneous γ-radiation	6
γ-quanta of decay	5
Delayed γ-quanta	5
Neutrino	11
Total	195

Figure 44 shows the arrangement of the chain reaction relative to U^{235} [491].

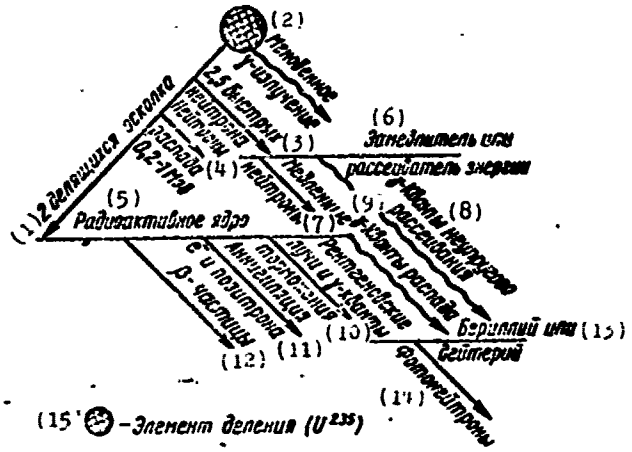


Fig. 44. The emergence of radiation in a reactor. KEY: (1) 2 fissionable fragments; (2) Instantaneous γ-radiation; (3) 2.5 fast neutrons; (4) Neutrons of decay, 0.2-1 MeV; (5) Radioactive nucleus; (6) Moderator or scatterer of energy; (7) Slow neutrons; (8) γ-quanta of nonelastic scattering; (9) γ-quanta of decay; (10) X-rays and γ-quanta of slowing down; (11) Annihilation of $\bar{e}$ and positron; (12) β-particles; (13) Berillium or deuteruim; (14) Photoneutrons; (15) Element of division (U^{235}).

The radiation field of a nuclear reactor. Let us examine briefly the contribution of individual components of reactor radiation during the irradiation of materials in the reactor core section.

The energy of neutrons obtained in fission reactions lies

basically in the area from 0 to 2 MeV, however, there are high-energy neutrons right up to 20 MeV [494, 495]. The energy distribution spectrum of neutrons is one of the most important factors during the irradiation of materials in a reactor because the energy of neutrons uniquily determines the probability of the reaction during their interaction with the material of the target (the object being irradiated).

In the examination of radiochemical effects with the participation of neutrons during the irradiation of materials in a nuclear reactor the radiation capture and absorption with the emission of charged particles are significant. Specifically, during the irradiation of hydrogenous materials by neutrons radiation capture in the reaction $H^1(n, \gamma)H^2$ makes a noticeable contribution to an increase in the flux of γ-quanta, and during the irradiation, for example of nitrogen-containing materials, the emission of charged particle in the reaction $N^{14}(n, p)C^{14}$ also leads to an increase in the share of absorbed energy.

The fission products nave atomic numbers of approximately 40 and 52 and mass of 97 and 137 respectively. Low speed and large mass limit the penetrating power of the fission products up to several micron in solids and liquids. The kinetic energy of the fission products (~80% of all the fission energy) is converted into heat energy.

The rate of emission of electrons by fission products during radioactive decay is approximately equal to

$$A = 3{,}8 \cdot 10^{-6} \cdot t^{-1{,}2}, \qquad (122)$$

where A - the rate of emission, *electron/s* per act of fission; t - time after division, days.

The main fraction of emitted electrons has an energy of ~0.4 MeV. A large part of emitted electrons is absorbed in the material of the nuclear fuel and it does not make a substantial contribution during the irradiation of materials in the field of a nuclear reactor.

The absorbed dose in the material being irradiated in the field of a nuclear reactor is conditioned basically by γ-radiation - instantaneous and delayed. The spectrum of γ-radiation of various reactors is examined in work [496].

Radiation modification with the utilization of reactors. The utilization of a significant fraction of fission energy which is carried off by γ-quanta and neutrons which are not participating in the chain reaction is very tempting, however, the practical utilization of this energy for the realization of industrial radiochemical processes, for example the modification of polymers, thus far runs into obstacles which are difficult to surmount (the appearance of induced radioactivity in the irradiated substance, significant temperatures within the limits of the core, and others).

The greatest part of fission energy is converted into the kinetic energy of fragments, therefore both in the USSR and abroad possibilities of the utilization of this energy are being investigated intensively. In connection with the very small ranges the use of fission products for the modification of polymeric materials has not been successful, however, realization of chemical reactions (synthesis for example) is possible with the help of the direct contact of the reaction mixture and the nuclear fuel. The realization of this so-called "chemonuclear synthesis" in industrial scales is a promising trend of the utilization of nuclear radiation in radiochemical processes; however, this path is also connected with certain difficulties (specifically the products of chemonuclear synthesis, which

contain partially the products of fission, are radioactive and must be purified thoroughly).

The irradiation of materials and products directly in the reactor core is not the only path for the utilization of fission energy. Today at least two additional possibilities exist.

The first of them consists of the utilization of the fuel elements of the reactor [tvel] (твэл) which have exhausted the run as the radiation sources. Fuel elements irradiated in a reactor possess high radioactivity both as a result of the neutron activation and due to the accumulation in them of radioactive fission products. Prior to technical treatment for the purpose of regeneration of unused nuclear fuel the fuel elements are stored in order to lower their activity as a result of radioactive decay and during this period they can be used as sources of γ-radiation for radiochemical processes. The average energy of γ-radiation of fuel elements is 0.7 MeV, and their activity drops quite rapidly with time. Therefore the utilization of fuel elements in installations for irradiation stipulates a quite frequent overloading which is coupled with certain inconveniences [497-500].

As the basis for the second possibility lies the original idea of the "yield" of radiation from the reactor core by means of the creation of a circulation circuit, the working substand in which are liquid-metal alloys made from elements with a large neutron capture cross section and a small half-life (In-Ga-Sn, In-Ga, etc.). The working substand, flowing between the core and the reflector of the reactor, is activated due to the absorption of neutron leakage and it makes it possible to create a source of γ-radiation of high effectiveness outside the limits of the reactor.

Radiation circuits have been constructed abroad and in the USSR (Gruzinskaya and Latviyskaya AN SSR) and they are used for

scientific-research purposes and for conducting experiments which model radiochemical processes [501-503].

Calculation shows that with a thermal neutron flux of $1 \cdot 10^{12}$ *neutron*/($cm^2 \cdot s$) the total power of the radiation circuit is 50 kW (~$5 \cdot 10^{33}$ gram-equivalent of radium). The annual productivity of the radiation circuit (Q t/yr) is equal to

$$Q = \frac{30w \cdot \eta}{D}, \qquad (123)$$

where w - power of γ-radiation, kW; η - efficiency of apparatus on γ-radiation, %; D - absorbed dose, Mrad.

In the modification of polyethylene (D = 100 Mrad, η = 25% and operating time - 4500 h) the annual productivity of the radiation circuit comprises approximately 200 t/yr.

Apparently such a process can compete with the irradiation of polyethylene on cobalt sources.

Radiation circuits have a series of substantial advantages as compared with γ-sources on the basis of long-lined isotopes [504-505]: 1) the possibility of regulating the activity over a wide range of dose rates with the help of a change in the rate of circulation of the working substance; 2) the ease of changing the configuration of the irradiator relative to the specifics of the product being irradiated; 3) the rapid drop in activity with termination of circulation of the working substance.

Furthermore the use of radiation circuits considerably raises the factor of utilization of reactor power.

The advantages of radiation circuits noted above show the promise of their utilization for the realization of large-capacity industrial radiochemical processes.

Isotope Sources of Ionizing Radiations

Among the numerous isotope sources of ionizing radiations put out by nuclear industry, the one used most is the isotope Co^{60} [504-507], obtained in nuclear reactors from metallic chemically pure cobalt:

$$_{27}Co^{59}(n, \gamma)_{27}Co^{60}.$$

With the subsequent radioactive decay of cobalt (the half-life is 5.3 years) two γ-quanta with energies of 1.33 and 1.17 MeV are emitted.

There is also a certain interest in sources from Cs^{137} (energy of γ-quanta 0.66 Mev, period of half-life - 33 years).

Soviet industry produces standard cobalt sources with an activity of 5-3000 g-equiv of radium. Cobalt sources have been ampulated into airtight aluminum or steel (from stainless steel) casings.

From the standard sources irradiators of different configuration relative to concrete radiochemical processes are collected. Most widely used are irradiators assembled in the form of a hollow cylinder ("squirrel wheel") or plane. The first type of irradiators make it possible to obtain a high dose rate in the inner cavity of the irradiator; it is advantageous to use flat irradiators during the conveyer transport of materials through the radiation zone.

The constructional fulfillment of isotope installations is very diverse [504, 506-509]. They are distinguished by the type of biological shielding in the case of an idle source (concrete, water, and others), the methods of converting the source from idle to working (electromagnetic, pneumatic, mechanical), and others.

Despite the significant diversity of isotope installations (based on the configuration of irradiator, the type of shielding, and others), the principle of their constructional fulfillment is sufficiently simple and, as a rule, is determined by the features of the radiochemical technology relative to which they have been developed.

As an example let us examine the construction of the K-20,000 installation (source activity - 20,000 g-equiv of radium), created at the NIFKhI imeni L. Ya. Karpov [NIFKhI-Physicochemical Sci-Res. Institute] [504-505]. In this installation a variant of "dry" shielding has been accepted. In the storage position the source is located in a special lead container; in the working position, when source has been withdrawn from the container, shielding is accomplished by concrete walls and a labyrinth entrance. The irradiator of the installation is a hollow cylinder with a height of 190 cm and outside diameter of 140 mm, and it contains 56 standard cylindrical preparations of Co^{60}. The average dose rate in the center of the irradiator is ~1100 r/s.

Given below are the technical data for isotope gamma-installations at the NIFKhI imeni L. Ya. Karpov which are utilized for conducting radiochemical processes of large scales.

Characteristics of irradiator	Type of installation.		
	K-200	KP-140	KSV-500
Activity, g-equiv of radium	200,000	190,000	530,000
Number of preparations, pcs.	160	140	220
Maximum specific activity of preparation, g-equiv of radium	35	70	90
Maxium dose rate, r/s	350	2,000	400
Method of movement of source	Electromagnetic	Pneumatic	Mechanical

The utilization of isotope γ-sources of ionizing radiations is advantageous during the irradiation of massive objects of complex shape, in which the creation of a uniform filed of absorbed doses in the case of corpuscular emission is hindered in practice or generally unattainable.

However, in a number of cases, for example during the irradiation of cable products with poliolefin insulation, the use of isotope gamma-installations is combined with some difficulties of a technical order due to the low dose rates of irradiation[1] (in this case irradiation has to be connected in an inert atmosphere or a vacuum for the prevention of oxidation during irradiation); at the required absorbed doses of ~100 Mrad the time for processing is very considerable; furthermore, the effectiveness of the utilization of radiation at an optimal geometry of irradiators is fairly low (20-30%).

Accelerators of Charged Particles

The charged-particle accelerators make it possible in principle to obtain high-energy bundles of any charged particles, however, when selecting the type of corpuscular emission for the radiation modification of the polymers the guiding factors are the penetrating power of the particles of a given form in the material being irradiated. Therefore fast electrons due to their high penetrating power are the only industrially utilized type of radiation.

The maximum depth of penetration of electrons into a material with an unitary density, expressed in centimeters, is equal approximately to half of the energy expressed in megaelectronvolts, i.e., electrons with an energy of 4 MeV can penetrate in water

[1]The creation of high dose rates in a large volume is possible in principle even when using γ-sources, but this is combined with significant technical difficulties.

to a distance of approximately 2 cm (the run of heavy charged particles - protons, α-particles, and other ions - with this same energy is several microns).

The fast electrons generated by accelerators can be used to obtain X-rays, but the maximum effectiveness of conversion at energies up to 3-4 MeV does not exceed 10% and the radiation intensity correspondingly drops.

There are many types of high-energy electron accelerators which are distinguished by operational and constructional features. Accelerators divided into two groups: accelerators of direct and indirect action.

The direct action accelerators are those, in which the accelerated particle acquires total energy during a single passage of the high-voltage interval. The energy of the electron in such an accelerator, expressed in megaelectronvolts, is numerically equal to the potential difference of the accelerating tube in megavolts. The maximum value of electrical voltage (and correspondingly the energy of electrons) which can be obtained on a direct action accelerator is determined by the electrical strength of the accelerator tube and other structural elements. The direct action accelerators include the electrostatic generator (Van de Graaf accelerator), resonance transformer, dynamitron, and others.

The accelerators of indirect action are those in which the accelerated particle traverses the accelerating gaps many times, gradually accumulating small quanta of energy.[1] Depending on the

[1] In this case the complete energy of the accelerated particle is determined not only by the magnitude of voltage applied on the acceleration interval, but also by the number of passages through the interval.

trajectory of the accelerated particle this group of accelerators is divided into cyclic (spiral or circular path) and linear (straight path) accelerators. Acceleratrs of indirect action include the cyclotron, betatron, synchrotron, linear accelerator, and others.

For the realization of industrial radiochemical processes the greatest interest lies in three types of accelerators - electrostatic generator, resonance transformer, and linear accelerator.

The descriptions of accelerators of various types are covered in a large number of works and monographs [510-516].

Electrostatic generator. The electrostatic generator, which was proposed in 1931 by Van de Graaf, is the most widespread direct action accelerator. It is used extensively both in physical experiments and in clinical therapy, industrial radiography, and also for radiochemical investigations, the fundamental range of energy of this type of accelerator is 0.5-5 MeV. According to works [517, 518] the distribution of electrostatic generators according to use in 1962 was the following:

Nuclear research	240
Clinical therapy	40
Industrial radiography	20
Radiation investigations	75
Altogether	375

The principle of operation of electrostatic generator (Fig. 45) is sufficiently simple: a belt conveyor, insulated from the earth, transfers an electric charge from a charging device to a high-voltage electrode. Near the lower pulley onto the surface of the transporter belt a charge from a high-voltage source will be applied. Its magnitude is doubled with the help

of a recharging device; the upper pulley is located under a high-voltage dome - the conductor - and it is found under the total voltage developed by the generator. The high-voltage acceleration tube, which consists of the electron source (the cathode) and an electron-optical system for beam focussing, is usually arranged vertically, next to the conveyor belt; the whole system is placed into a metallic tank filled with a mixture of CO_2 and N_2 or SF_6 under a pressure up to 30 kgf/cm^2 for suppression of corona discharge.

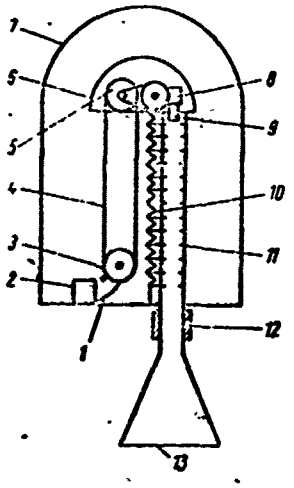


Fig. 45. The arrangement of a electrostatic generator: 1 - charging comb; 2 - power pack; 3 - lower pulley; 4 - belt made from insulated material; 5 - upper pulley; 6 - metallic hemisphere; 7 - metal casting; 8 - power pack of the filament; 9 - filament; 10 - potential divider; 11 - evacuated accelerator tube; 12 - scanning coil; 13 - window for output of electrons.

The monochromatic electrons obtained on the electrostatic generator are focussed into bundle with an area of ~1 cm^2 with a Gaussian distribution of intensity along the diameter of bundle and are lead out from the vacuum high-voltage tube into atmosphere through an aluminum or titanium foil with a thickness of several tens of microns. In this case occurs the certain power loss of accelerated electrons.

In electrostatic generators the maximum current depends on the width and the speed of the conveyer belt. Usually this type of accelerator has a current on the order of 1 milliampere, although it is possible to achieve high currents. Therefore industrially produced accelerators of this type on an energy of

electrons up to 5 MeV have a power less than 5 kW.

Soviet industry produces electrostatic generators of different energy serially. The EG-2.5 electrostatic accelerator [316] has the following characteristics: operating voltage 1-2.5 MeV, current in a bundle ~250 μA. During pulsing it is possible to obtain considerably high currents.

Abroad the HVEC firm produces electrostatic generators intended especially for radiochemical investigations and processes [491]:

Energy, MeV	Current, in A
1.5	1.67
3.0	1.0
4.0	1.0

Electrostatic generators because of their mechanical features possess the following significant advantages: 1) the possibility of changing the accelerating voltage over a wide range; 2) the high stability of accelerating voltage and therefore energy homogeneity of the electron stream; 3) the possibility of utilization of the generator not only in a static, but also in a pulsed operation; 4) the possibility of changing the parameters of pulsed operation by using high-voltage electrodes of various geometric dimensions (change in the capacity of the system).

The peculiarities of electrostatic generators noted above condition the prospect of their use in industrial radiation processes.

Distortion transformer. In this type of accelerators the high-voltage generator is a low-frequency (50-180 Hz) transformer, into which a high-voltage accelerator tube is mounted coaxially. The transformer and the tube are placed into a metallic tank with compressed gas (freon, elegaz [Translator's note: Possibly -

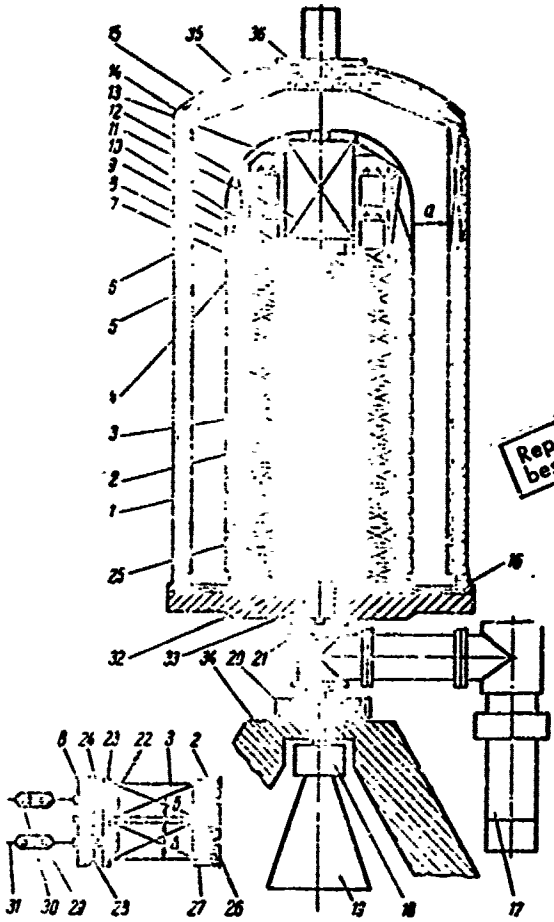
sul'ur hexafluoride] and others). Initially the resonance transformer was used for obtaining X-rays for theraputic purposes, and subsequently it began to be used as a source of electrons [519].

Figure 46 shows a cross section of a resonance transformer [515]. The latter consists of the primary and secondary winding, between which a magnetic circuit is arranged. The accelerator tube, arranged along the axis of transformer, is connected with the disks of the magnetic circuit. The electron injector has a control electrode. The power supply of the injector, the control electrode, and the cathode filament is accomplished by the application of voltage from part of the secondary winding. The capacitance divider is the sensor of the circuit for the automatic control of voltage.

The constance of accelerating voltage is attained by current regulation in the tube with the help of a change in potential on the control electrode of the injector: the voltage drop on the accelerator tube is deducted from the voltage applied to the tube of the secondary winding and under a specific law for a change in current through the tube constancy of accelerating voltage is ensured.

A mechanical analog of the resonance transformer is the rocking pendulum or the mechanical system, in which the mass vibrates into resonance with an elastic support. In such a mechanical system a small force with frequency equal to the natural frequency of the system at a relatively small power can maintain a large amplitude of oscillation.

The natural frequency of the high-voltage circuit of a resonance transformer is selected equal to the frequency of power-supplying voltage.



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Fig. 46. Constructional layout of a resonance transformer (E1T-1.5); 1 - primary winding of transformer; 2 - section of secondary winding; 3 - magnetic circuit disk; 4 - high-voltage part of magnetic circuit (head); 5, 6, 14 - parts of the magnetic circuit; 7 - coil of head; 8 - accelerator tube; 9 - control electrode; 10 - injector; 11 - power system for injector; 12 - capacitor bank; 13 - capacitance pickup of head; 15 - boiler; 16 - base of magnetic circuit; 17 - vacuum pump; 18 - turning magnet; 19 - funnel with delivery port; 20 - Rogovskiy belt; 21 - tester; 22 - copper rings; 23 - bearing cylinders; 24 - elastic contacts of accelerator tube; 25 - screen of primary winding; 26 - screens of sections of the secondary winding; 27 - protective gaps; 28 - ohmic divider; 29 - magnetic lens; 30 - radiation screens; 31 - electrodes for the accelerator tube; 32 - ball bearing for the tube; 33 - packing for the tube; 34 - radiation shielding; 35 - radiator for cooling; 36 - ventilator.

In the [ElT-1.5] (ЭлТ-1.5) accelerator, developed at the Institute of Nuclear Physics of the Siberian Department of the Academy of Sciences USSR, the natural frequency of the resonance transformer is equal to 50 Hz, and the power supply of the primary winding is accomplished directly from the network. In American installations [319, 320] they use a frequency of 180 Hz which is developed by a synchronous dynamotor. In this case the high frequency stability at assigned level is attained; thus for a generator on a voltage of 1 MV the frequency fluctuations lie within the limits of 180 ± 0.9 Hz, and for a generator on 2 MV - 180 ± 0.5 Hz.

The significant excess of pulsed power over average in resonance transformers does not reduce the possibilities of their use for radiochemical processes, because in the procedures developed for the irradiation of materials and products the required absorbed dose is collected additively from the large number of pulses.

ElT-1.5 installations [515] have the following parameters:

Supply voltage of primary winding, frequency	220/380 V, 50 Hz
Maximum voltage on the secondary winding in the mode of idling	1.7 MV
Range of change in accelerating voltage	0.4-1.5 MV
Average power of electron beam (V = 1.5 MV)	25 kW
Pulsed power of electron beam	150 kW
Average current under basic conditions	17 mA

Resonance transformers are produced by many foreign firms: Max Plank Institute (FRG) - an accelerator on 2 MeV, Toyo Rayon Co., Osaka (Japan) - an accelerator on 1 MeV, General Electric Co., (USA) - an accelerator on 1 MeV, and others.

As compared with direct action accelerators of other types the resonance transformer has the following advantages: 1) the automatic control of accelerating voltage and current in the beam; 2) high efficiency; 3) the possibility of obtaining an electron stream of high power; 4) the absence of moving parts.

Linear accelerators. The use of the method of direct acceleration of electrons on an energy higher than 5 MeV runs into ever increasing difficulties connected with providing for the insulation of the high-voltage parts of the accelerator, which in particular leads to an increase in dimensions which is not proportional to energy. As a result of this for industrial use accelerators of direct action on an energy greater than 5 MeV are not made, although unique samples for physical investigations exist in a number of countries.

Therefore electron beams with an energy higher than 5 MeV are obtained with the help of accelerators of indirect action - the so-called "linear resonance accelerators" [515, 521-523]. In a linear accelerator a high-frequency electric field is used which is applied to the linear periodic system of electrodes, the frequency of which is constant and it is found in resonance with the movement of particles. One and the same particle passes all the accelerating gaps at the same phase of electric field and is accelerated in every interval. The layout of a linear accelerator[1] is shown in Fig. 47.

Already at a comparatively low energy - 2 MeV - the speed of the electrons approaches the speed of light (~0.92 S) [S - speed of light], which makes it possible to make the distance between electrodes - adjacent accelerating gaps - identical. In linear accelerators usually waveguides with a running or standing wave are used.

[1]The principle of operation of linear accelerators is described in detail in work [513].

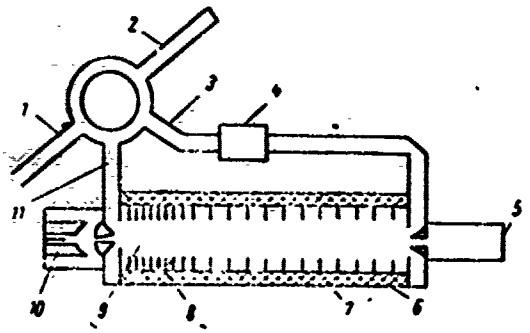


Fig. 47. The layout of a linear accelerator: 1 - input of high-frequency power; 2 - load; 3 - feedback; 4 - the shift of phase unit; 5 - the window for output of electrons; 6 - focusing coils; 7 - the area of energy storage by electrons; 8 - the area of beam shaping; 9 - wave guide; 10 - electron gun; 11 - power supply of wave guide.

In such a wave guide (right angled or circular section) the wave velocity of the running wave is equal to the speed of the electrons. The phase velocity of wave is equal to

$$v_ф = \frac{c}{\sqrt{1-\left(\frac{\lambda}{2a}\right)^2}}, \qquad (124)$$

where λ - the wavelength of the high-frequency field during its dissemination outside the wave guide; a - the maximum size of a section of the wave guide.

As can be seen from expression (124), the phase velocity of the wave proves to be greater than the speed of light. In order to lower this velocity to the speed of the electrons the wave guide is loaded with concentrated distributed reactive loads (usually ring diaphragms).

Minimal sizes and maximum quality of a wave guide can be obtained only at a sufficiently high frequency of electromagnetic vibrations, therefore as the source of high-frequency power a magnetron or klystron is used. The pulsed power of contemporary high-frequency generators reaches tens of thousands of kilowatts with a frequency of 3000 MHz and a pulse width of several microseconds.

The fundamental characteristics of linear accelerators of electrons produced in the USSR and abroad are noted below.

Energy, MeV	Average power kW	Source of high-frequency power	Producing firm
8	0.3	Magnetron	Metropoliten Vickers Electrical Co., Ltd.
14	0.45	Magnetron	
4	0.4	Magnetron	
2-10	1.3	Klystron	Millard Research Laboratories, Associated Electrical Industries, Ltd.
2-15	5.0	Klystron	
25	30.0	Klystron	
1.4-2	0.4	Magnetron.	Applied Radiation Corporation, Varian Associated Electrical Industries, MIFI, USSR [MIFI - Moscow Engineering Physics Institute].

Linear accelerators of electrons can be used in industrial radiochemical processes when it is necessary to irradiate massive objects up to significant absorbed doses. Furthermore these installations are of interest also as sources of hard x-radiation, since the conversion coefficient at energies of several tens of megaelectronvolts is already sufficiently great and at a power of bundle of tens of kilowatts such a transformation is technically and economically justified.

The brief description given above for the sources of ionizing radiations shows that today there is already a sufficient diversity of them both based on the form of radiation and on power. The fundamental technical-engineering problems in the creation of powerful radiation sources for industrial purposes have been solved to a considerable degree and work in this field continues to be developed intensively relative to the demands of developing radiochemical technology. The questions connected with the selection of one or another type of source for a specific radiochemical process taking into account all the specific features of technology and economy are examined below.

THE TECHNOLOGY OF RADIATION MODIFICATION

The principles of selection of the sources of ionizing radiation. The radiation source for an industrial radiochemical process is selected taking into account many factors, the main of which are the following: 1) the necessary irradiation dose; 2) the productivity of the process; 3) economic effectiveness of irradiation.

The first two factors determine the power of the radiation source. Since in most cases it is not possible to use radiant energy completely, during the determination of source intensity it is necessary to introduce the radiation utilization factor. The radiant energy does not enter into this examination because it is selected or the strength of the penetrating power of radiation of the given form taking into account the providing of optimal distribution of dose field in the bulk of the irradiated object.

The economic effectiveness of the utilization of ionizing radiations for the conducting of radiochemical processes depends on the following factors [546-548]: 1) radiochemical reaction yield; 2) the cost 1 kWh of radiant energy; 3) the radiation utilization factor; 4) the volume of production.

As already mentioned, a necessary requirement for the technology of the radiation processing of materials in general, and cable polymeric insulation especially, is the homogeneity of the modified material in its entire volume, which it is possible to achieve only under the condition of evenness of the field of absorbed doses.

The radiation processing of polymers for the achievement of the necessary operating characteristics can be carried out on finished products because the polymeric materials subject to

irradiation lose their manufacturability, they cannot be reworked into products by the methods of extrusion, molding, milling, etc.

At the same time the irradiation of cable products in finished form (or semi-finished goods) for the purpose of the radiation modification of polymeric (for instance, polyethylene) insulation presents significant difficulties because cable products are typical heterogeneous systems.

Furthermore a very substantial requirement in the creation of an economically advantageous radiation process is the achievement of the maximum effectiveness of the utilization of radiant energy.

Apart from these general requirements, the use of one or another type of radiation source taking into account its power and other characteristics gives rise to the necessity for the solution of a number of accompanying problems - the selection of the medium for irradiation, the providing of heat withdrawal, etc.

Independent of the form of radiation source used in the organization of an industrial radiochemical process some general requirements should be fulfilled: the building of a special installation for the accomodation of the radiation sources and industrial equipment; the ensuring of the radiation safety of service personnel; the reliability of the system of signaling and blocking, etc. These problems are reflected sufficiently fully in a number of investigations [524; 525].

All this naturally considerably limits the constructive formation of the procedure of radiation processing of cable and electrical insulation products.

At the same time for various types of ionizing radiation - γ-radiation and electron - the technology of radiation modification is substantially different from one another, therefore they will be presented separately.

Let us examine briefly the fundamental parameters and the positive solutions realized on industrial and research-and-development installations for the radiation modification of wires and cables with polymeric coverings and some other electrical insulating products.

The Technology of Radiation Modification on Isotope Sources

Intensively conducted investigations for the purpose of realization on industrial scales of a number of radiochemical processes on isotope installations (the cross-linking of polyethylene, the vulcanization of rubbers, the modification of wood, and others) led to the working out of general physical engineering methods of calculation of the fundamental parameters of radiochemical apparatuses [526-530] and made it possible to determine the influence of various geometric parameters of an installation on the effectiveness of utilization of radiation [531-541].

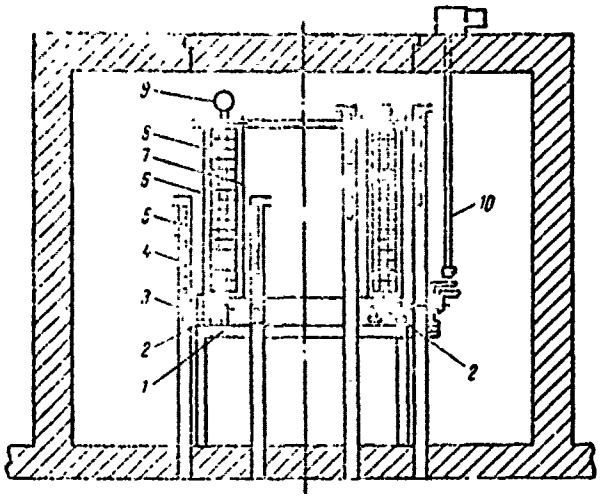
Furthermore relative to specific radiochemical processes optimal parameters have been proposed for isotope installations [542-545].

On the installations described in literature for the conducting of radiochemical processes on enlarged and industrial scales with the help of γ-radiation basically irradiators from preparations of Co^{60} or waste fuel elements are used.

For the irradiation of wires and cables with polyethylene insulation the authros of work [545] used a cobalt irradiator

assembled in the form of two concentric arcs with radii of 100 and 105 cm. The radiochemical apparatus for irradiation was an annular cylindrical vessel (average radius 105 cm), into which a coil with a cable (wire) wound on it was inserted. This vessel was hermetically sealed and after vacuuming filled with an inert gas (helium). For the creation of an uniform field of absorbed doses the thickness of the cable winding was selected taking into account the absorption of the polymer - copper system, and the apparatus was rotated around a vertical axis. At an activity of irradiators of 50,000 g-equiv of radium and an utilized height of 26 cm the average power of absorbed dose comprised 52 rad/s with a nonuniformity of irradiation of ±10%; at an irradiation dose of 100 Mrad the productivity of the apparatus reached 0.1 kg/h and efficiency (the utilization of radiation) ~3.5%.

For increasing the coefficient of radiation utilization and productivity of the installation a method of sectional irradiation was developed which was realized on a KSV-500 isotope gamma-installation with an activity of 500,000 g-equiv of radium (Fig. 48). Into this installation into the cylindrical irradiator an apparatus was placed and concentric coils with the cable (three series) were loaded into it. In this case it was possible with the help of the special apportionment of the preparations of Cobalt to use 85% of the height of the irradiators for irradiation. The sectional method gives rise to a different exposure time for every coil, however, within the limits of one coil with the appropriate selection of the thickness of winding the field of the absorbed doses has a scattering of no more than ±10%, and the coefficient of utilization and productivity of the apparatus increases considerably (η = 12%, Q = 1.2 kg/h), despite the necessity for manifold overloading with subsequent sealing and vacuuming.



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Fig. 48. The layout of an apparatus for the radiation cross-linking of cable products: 1 - working table; 2 - bearings; 3 - piston-push rod; 4 - channel for irradiator; 5 - sources; 6 - apparatus; 7 - coil; 8 - cable; 9 - vacuum manometer; 10 - drive.

Both the positive solutions described possess the shortcoming that the dimensions of the drum on which the cable (wire) is wound are limited by the configuration of the irradiator, which gives rise to the necessity for the irradiation of cables in comparatively small structural lengths (for instance, on the first apparatus the capacity of the drum for a cable with a diameter of 6 mm does not exceed 800 m). This deficiency was overcome to a considerable extent by the construction of an apparatus of a KP-200 installation. The stepped disposition of sources in the irradiator made it possible to increase its height up to ~150 cm. The equalization of the field of absorbed doses on the perimeter of the apparatus was accomplished by means of the partial screening of the middle part of the sources by lead filters, by the alignment of the disposition of the irradiators, and with the help of rotation of the apparatus around the vertical axis. The average power of absorbed dose comprised; ~63 rad/s, η = 13%, and Q = 0.9 kg/h at an irradiation dose of 100 Mrad.

Despite the individual constructional differences, which substantially influence the technical-economical characteristics

of the process, all three described installations unite the following general features (with the vertical orientation of the axis of the apparatus): 1) the use of cylindrical irradiators; 2) the achievement of uniformity in the field of absorbed doses with the help of the appropriate selection of winding thickness, two-sided irradiation (horizontal uniformity), and by a special choice, by the partial screening of the irradiators, and also by the rotation of the apparatus around the vertical axis (vertical uniformity).

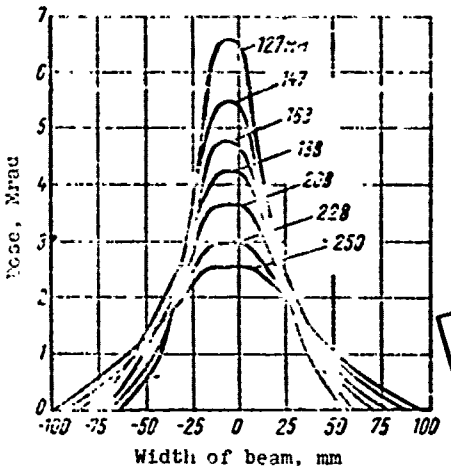
It is necessary to note that the described solutions for the technology of irradiation of cable products are not uniquely possible. Thus there is interest in the utilization of sector flat irradiators which, apparently, in certain cases more suitable for the irradiation of cables and wires.

The irradiation of polymeric tubes and films by Co^{60} γ-radiation is less difficult (homogeneous system) and can be conducted on the described installations with a considerably greater coefficient of utilization of radiation and productivity.

The Technology of Radiation Modification on Accelerators of Charged Particles

The specifics of beam of accelerated electrons applies definite requirements also on the technology of radiation modification.

As was noted above, the focused electron beam after exit from the discharge port of the accelerator has a circular cross section with a Gaussian distribution of intensity of radiation (and respectively the dose in the irradiated object) along the diameter. With removal from the port the scattering of the electron beam in the air occurs, which gives rise to a decrease in energy and a change in the distribution of intensity (Fig. 49)



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Fig. 49. The scattering of electron stream in air depending on distance (shown on curves) from the discharge port.

in a cross section of the beam. The utilization of the area of an immobile beam in the case of providing a uniformity of dose field in the irradiated material within the limits of ±20% is very low - no more than 50% (Fig. 50a). Furthermore at the very high dose rates which are created by contemporary accelerators the energy concentration or a small area creates considerable difficulties in providing for heat withdrawal both from the material of the discharge port and from the irradiated object itself. At a dose rate of 1 Mrad/s the amount of required energy comprises 10 W/g, or 24 Cal/(g·s), which for many plastics gives rise to an increase in temperature by 5-6°C in 1 s.

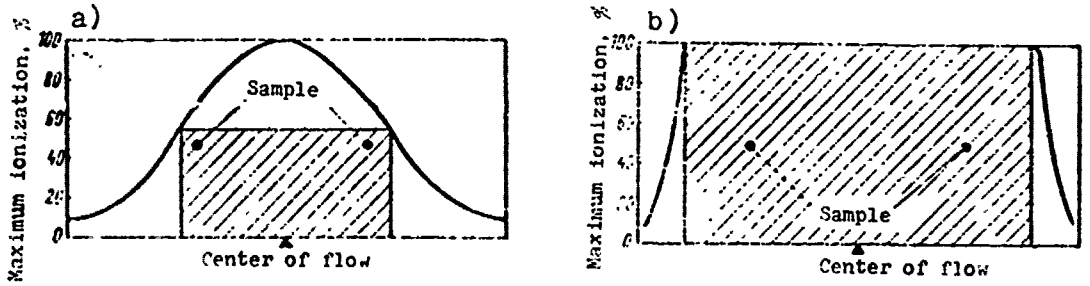


Fig. 50. The horizontal distribution of intensity of flow for nonscanned a) and scanned b) electron beams.

For increasing the utilization factor of the electron flux and dispersal of the absorbed energy the electron beam is rolled out (scanned) with the help of a magnetic or electrical field into two mutually perpendicular directions analogous to frame scanning in a television set. The scanning frequency is selected depending on the structural features of the accelerator, but no lower than hundreds of oscillations per second. Therefore for practical purposes the scanned electron flux can be considered as a certain average flow on the entire area of scan.

With this the utilization factor of the beam area can be increased to 90% (Fig. 50b), and heat transfer is simplified.

The penetrating power of electrons in a material is approximately directly proportional to the energy of the electrons (above 1 MeV) and inversely proportional to the density of the material. Figure 51 shows the dependence of relative absorbed dose for a monoenergetic electron stream on the depth of penetration referred to the energy of electrons (in the range of energy of electrons 0.5-10 MeV), and in Fig. 52 - the dependence of relative ionization on the thickness of the layer of water for electrons of different energies.

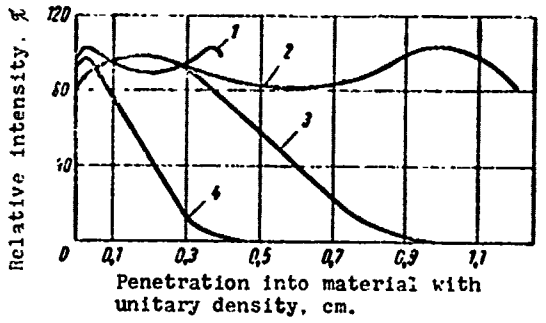
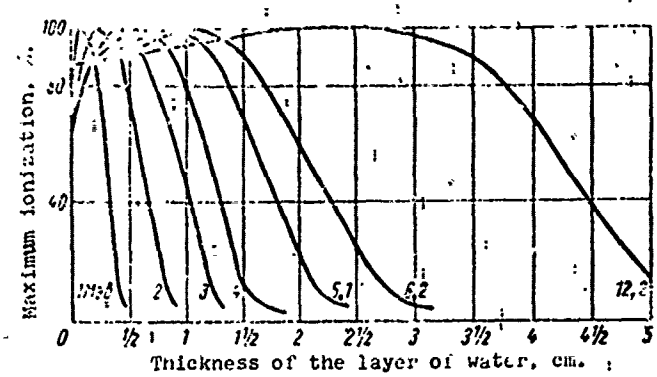


Fig. 51. The distribution of intensity of flow in the depth of material: 1 - two-sided irradiation, 1 MeV; 2 - two-sided irradiation, 2 MeV; 3 - one-sided irradiation, 2 MeV; 4 - one-sided irradiation, 1 MeV.



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Fig. 52. The distribution of ionization in the thickness of water.

It is evident from the given dependences that the absorbed dose is extremely unhomogeneous in the depth of the material. Furthermore the complexity of irradiation by electron flow of fine, for example film, materials becomes obvious because the maximum of ionization usually corresponds to one third of the maximum depth of penetration of electrons of a given energy. The utilization factor of radiation in depth at the optimal energy of electrons for ensuring the uniformity of irradiation dose within the limits of ±20% does not exceed 60-70% with one-sided irradiation and can reach 80% during two-sided irradiation of a flat object of uniform thickness (Fig. 53).

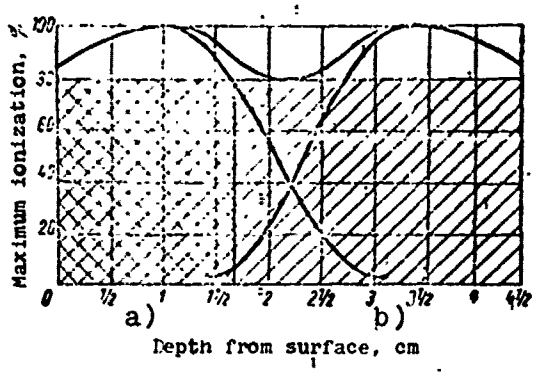


Fig. 53. Distribution of ionization in the thickness of material during one-sided a) and two-sided b) irradiation.

The summary utilization factor of the energy of an electron beam will be equal to the product of the utilization factor of the beam area by the utilization factor of the beam in depth. The irradiation of objects of a complex shape or unhomogeneous by high-energy electrons is combined with significant difficulties. Thus, during the irradiation of an insulated current-carrying core it is necessary to take into account both the diverse thickness of the insulation layer for the electron flux and the screening effect of current-carrying core (Fig. 54). Therefore the two-sided irradiation of the core (for the elimination of screening) does not eliminate the nonuniformity of the field of absorbed doses even with the appropriate selection of the energy of electrons (Table 42) [546].

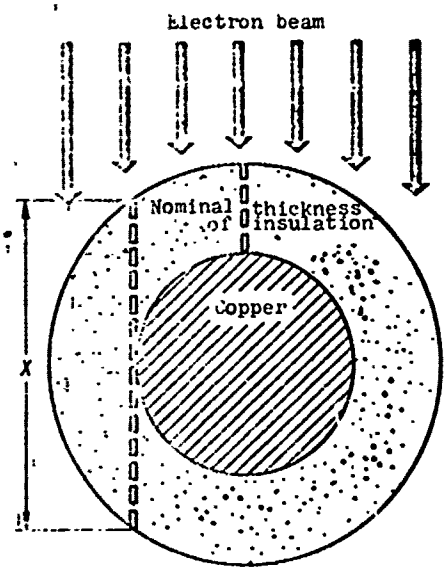


Fig. 54. Diagram of the cross section of a wire coated with plastic which shows the maximum depth of insulation (X) which must be taken into account when establishing the irradiation dose utilized if the wire is not rotated. The nominal thickness of insulation is equal to $\frac{D-d}{2}$. The greatest thickness of insulation $\sqrt{2(D^2-d^2)}$, where D - the diameter of the wire with insulation; d - without insulation.

The optimal distribution of the field of absorbed doses can be achieved by the two-sided irradiation of a cable product by two beams of accelerated electrons arranged at an angle of 90° to one another [461].

Table 42. The limitations on the energy of an electron flux and the dimensions of wire for two-sided irradiation.

Energy	Thickness of insulation, mm.	Dimensions of conductor
40-75 keV	0.635	0.66-2.44 mm or from 22 to 11 caliber
150-300 keV	1.27	1.27-4.83 mm or from 16 to 5 caliber
0.75-1 MeV	2.54	4.07-7.62 mm or from 6 to 1 caliber
1.5-2 MeV	3.81	4.57-8.13 mm or from 5 to 0 caliber
3-3.5 MeV	5.08	8.1-11.2 mm or from 0 to 000 caliber

Note. Energy depends to a high degree both on the thickness of insulation and on the dimensions of the conductor. Every threshold of energy encompasses a group of insulated wire with the approximate relationship of the thickness of insulation to the dimensions of the conductor from 1:1 to 1:3.

In order to ensure the two-sided irradiation of cable products, they are passed many times under a scanned beam, each time changing their orientation with respect to the beam by 180° with the help of a special attachment. A method has been proposed for the rotation of the wire under the beam which is combined with some technical difficulties, but considerably raises the utilization factor of the radiation [491].

A certain increases in the effectiveness of utilization of radiation during the irradiation of cables and wires can be achieved by the sloping disposition of parts in respect to the beam (an increase in the effective thickness of insulation) [546].

The technology of irradiation of polymeric electrical insulating tubes (both for raising their heating stability and for gaining the properties of thermal setting) is not substantially different from the irradiation of cables and wires because also in this case the diverse thickness of the object is retained. True the screening effect created in wires and cables of the current-carrying core is absent.

It is possible to irradiate film material by two technical methods - by winding (by reeling) the film on a drum under the beam or uninterrupted transporting during multiple traversal under the beam. Both methods lead to a sufficient uniformity of the filed of absorption of doses and high effectiveness in the utilization of radiant energy [546].

Although fundamental approach to the solution of the problem of industrial irradiation of wires and cables with polymeric insulation, as also a number of auxiliary materials, was discussed widely and is sufficiently clear at the present time, and in a number of countries the process of radiation modification of polymers is already accomplished on multiton industrial scales, in the literature the description of the industrial processes realized is absent, which is apparently connected with situation considerations. Therefore, unfortunately in the literature such substantial questions of radiation technology of the modification of polymers as heat transfer from the irradiated product, the industrial use of methods of sensitization of the process, and others have not been illuminated.

The Comparison of Various Types of the Sources of Ionizing Radiations and Some Technical-Economical Evaluations

On the basis of the above examination of the fundamental features of the characteristics of radiation sources of various types it is possible to compare them from the point of view of the worthwhileness of use for some concrete process.

Today experience in the utilization of nuclear reactors for the modification of polymers is practically absent. At the same time both in the USSR and abroad already a certain experience has been accumulated in the use on laboratory and enlarged scales of isotope sources of γ-radiation and electron accelerators of

various types in the radiation chemistry of polymers, and this makes it possible to draw some general conclusions.

As a result of the analysis of the specific features of the field pattern of radiation, the penetrating power of radiation, the realizable dose rates, and other factors, including simplicity and the ease of handling, the necessary qualification of personnel, etc., it is possible to make the conclusion that from general consideration preference cannot be given to sources of ionizing radiation of any specific type.

Really both the sources of γ-radiation and electron accelerators have their inherent pros and cons. Let us examine some of them.

As advantages for installations with sources of γ-radiation the following can be attributed: 1) the possibility of obtaining an uniform field of absorbed doses in a large volume of homogeneous material; 2) the possibility of the irradiation of objects of complex shape with acceptable nonuniformity based on the absorbed dose; 3) the comparative simplicity of construction; 4) high reliability; 5) relatively low requirements for the qualification of maintenance personnel; 6) the relative simplicity of irradiation of products in the required atmosphere.

Their shortcomings are: 1) the difficulty of obtaining a high dose rate in a sufficiently large volume; 2) the necessity for the periodic making up of the natural decrease of activity of the γ-source as a result of radioactive decay; 3) the comparatively low utilization factor of radiation; 4) the presence of radiation hazards outside of the dependence on whether or not the source is used and the possibility of radioactive contamination.

The advantages of installations with electron accelerators include: 1) the possibility of obtaining a high dose rate; 2) a high radiation utilization factor; 3) the absence of radiation

hazards (with a nonworking installation) and radiation contaminations; 4) the simplicity of control of the parameters of the radiation field.

The shortcomings of installations with accelerators are: 1) the difficulty of providing a uniformity of the field of absorbed doses in the irradiated object; 2) significant heat liberation in the irradiated object and the necessity for solving the problem of heat transfer; 3) the significant complexity in the arrangement of the accelerator itself; 4) relatively less reliability during exploitation; 5) the necessity for the highly skilled maintenance personnel.

Such a comparison of advantages and shortcomings in the radiation sources of various types still does not give a complete presentation about the expediency of using one of them. Let us compare the pros and cons of sources of these types relative to the process of radiation modification of polymeric ins lation in cable products.

Cable products as objects for irradiation are characterized by a number of specific features: 1) they are a typically heterogeneous system (current-carrying core and insulation) with a low polymer - metal ratio; 2) large lengths with small outside diameters; 3) capacity for oxidation upon heating and irradiation in the air.

Furthermore, because of the unique geometry of cable products it is advantageous to carry out all technological processes with rewinding (which is also generally accepted in conventional cable technology).

Since the average irradiation dose for polymeric insulation of cable products which is necessary for modification is sufficiently sufficiently great and comprises 50-100 Mrad, for obtaining an

acceptable productivity of the installation a high dose rate is required.

The impossibility of the realization of this requirement in a large volume on an isotope source leads not only to low productivity of the installation, but also to the necessity for carrying out the process in hermetically sealed vessel filled with an inert medium (for the prevention of radiochemical oxidation), i.e., to a basically periodic process and limited lengths of cable products being processed.

In this respect an installation with an electron accelerator corresponds more to the specifics of cable technology. The high dose rates in an electron beam make it possible to conduct the radiation processing of the polymeric insulation of cable products directly during its passing through the radiation zone. In connection with the short duration of stay of the cable product under the beam the influence of the process of radiation oxidation of insulation diminishes. At the same time the presence of a high dose rate in conjunction with the low thermal conductivity of the polymeric insulation advances to the foreground the problem of heat extraction from the irradiated product.

Even such a brief review shows that a rational procedure should be constructed taking into account many factors which consider the features both of the radiation source and the product being irradiated, and the radiation source has to be selected on the basis of an analysis not only of engineering problems, but also the technical-economical effectiveness of the process.

The comparatively little experience in the utilization of radiation installations in technological processes did not make it possible to accumulate a sufficient quantity of data for a detailed economic analysis. At the same time in the literature there are some results of cost estimates of irradiation on various installations.

The data present in the literature [546-560] which characterize the cost of 1 kWh of energy of ionizing radiation of various radiation sources are sufficiently contradictory, and since they relate to sources of various types of radiations which differ strongly in power, energy, etc., they should be treated with a certain caution. In Table 43 some data are given on the cost of 1 kWh of energy of radiation.

Table 43. Cost of 1 kWh of radiant energy

Source of ionizing radiation	Power, kW	Activity, MCu.	Cost, 1 kWh dollar	Literature
Electrostatic generator	5-25	-	1	[550]
Linear accelerator	3	-	5.2	[551]
Resonance transformer	10	-	5	[552]
Electrostatic generator	3	-	0.5	[552]
Co^{60}	3	0.2	8.7	[553, 554]
Co^{60}	3	0.2	6.09	[555]
Co^{60}	3	0.2	9	[556]

It is necessary to emphasize that the comparison of the cost of radiation of γ-sources and accelerators is sufficiently conditional because the selling price of radioactive preparations (Co^{60}, Cs^{137}, fuel elements) is not determined at all from commercial consideration.

More admissible is a comparison of the cost of radiant energy within the framework of one and the same type of radiation source - isotope sources and accelerators of charged particles.

The cost of any type of radiation installation is made up of the cost of the building, the radiation source itself, and industrial equipment. However, the relationship between these values for various types of sources are different, and within

the framework of one and the same type depends on the power of the installation and other factors.

Thus, according to work [506] for cobalt isotope installations with a source activity of an order of 10^6 g-equiv of radium the expenditures for the structure make up more than half the outlay for the installation. For more powerful installations (source activity of 10^7 g-equiv of radium and higher) the fundamental contribution to the major expenditures is conditioned by the cost of the sources. A substantial component of the cost of irradiation on cobalt installations are expenditures for the yearly making up of the decrease of the source activity because of natural radioactive decay, because otherwise the productivity of the installation will continuously diminish.

For direct action accelerators - electrostatic generator and resonance transformer - with an increase in the energy of electrons there is a sharp increase in capital expenses for the basic equipment. An analysis of the dependence of capital outlays for basic equipment on the energy of the beam [591] shows that as a rule the output of an installation increases considerably more slowly than capital outlays.

In Table 44 a rough estimate is given of the cost of radiation on a resonance transformer based on materials of work [557]. However, even for one and the same type of accelerator the cost of the radiation process depends on the concrete parameters of the latter, and for one and the same process - on the power of accelerator; in this case with an increase in the power of the accelerator the cost of radiation processing can both increase and decrease (Table 45) [558-560].

Let us evaluate tentatively by how much the cost of a cable product with polyolefin insulation will increase because of the introduction of radiation modification.

Table 44. The calculation of the cost of a radiation process with the use of a resonance transformer of 2 MeV, 10 kW.

Article of expense	Cost	
	General, dollar	Specific*, dollar/h
Accelerator (resonance transformer)	120,000	5.0**
Construction (40% of cost of machine)	48,000	1.2**
Industrial equipment (15% of cost)	18,000	0.45**
Accelerator tube	13,000	3.25***
Reserve parts, etc.	4,000	0.5*
Servicing	-	2.75
Electric energy**** (installed capacity 50 kW).	-	0.25
Gain		4.19
Altogether		15.59

*Calculated on 8000 h/yr operation.
**Calculated on a 5-year amortization.
***Calculated on 4000 h of work (guarantee 1000 h).
****Calculated at a cost of 0.5 cents for 1 kWh.

Table 45. The cost of radiation processes with the use of linear accelerators.

Process	Dose, rads	Utilization factor, %	4 Mev, 0.6 kW (magnetron)		4 MeV, 5 kW (klystron)	
			Productivity	Cost of Processing	Productivity	Cost of processing
Protection of potatoes from germination	10^4	30	11 t/h	11/9 $/t	90 t/h	1/6 $/t
Sterilization of foodstuffs	$5 \cdot 10^4$	45	4,32 lb/h	1/2 $/lb	16 t/h	8/6 $/lb
	$5 \cdot 10^3$	45	432 lb/h	41/2 $/lb	3600 lb/h	1/2 $/lb
Vulcanization of rubbers	$5 \cdot 10^6$	80 (Without packing)	77 lb/h	1/8 $/lb	640 lb/h	21/2 $/lb
		25 (in products)	24 t/h	5/3 $/lb	200 lb/h	8 $/lb
Processing of plastics	$25 \cdot 10^6$	25 (in products)	5 lb/h	25 $/lb	40 lb/h	3/4 $/lb

As can be seen from Table 44, the cost of irradiation on a resonance transformer with an energy of 2 MeV and power of 10 kW is ~15.6 dol/h. It is known that during irradiation up to a dose of 100 Mrad with a 100% utilization of a radiant energy the productivity based on polyethylene comprises 3.6 kg/h [546]. Therefore in one hour on such an accelerator it is possible to irradiate 36 kg of polyethylene and the cost of irradiation will comprise $\frac{15.6}{36}$ = 0.5 dol/hr. Let us assume that the coefficient of utilization of radiation comprises 70%, then the cost of irradiation will be 0.7 dol/kg. On the strength of the existing rate of exchange (1 dol = 90 kopecks) the cost of irradiation of 1 kg of polyethylene will be equal to 60 kopecks. This shows that as a result of irradiation the cost of polyethylene is doubled. If one considers that in the total cost of cable product the cost of the insulation is low, then radiation modification does not substantially raise the price of the part. Even in the case of wire leads (average expenditure of polyethylene 1 kg/km, cost 6 rubles/km) the increase in price will not exceed 10%.

However one ought to note that the radiation modification of polyethylene insulation in cable products adds to them essentially completely new qualities and makes it possible to use them under those operating conditions under which the nonirradiated polymer cannot be used, and therefore the comparison of the cost of irradiated and nonirradiated polymer is unequal.

Therefore the economic advantage of the use of methods of radiation modification in most cases must be determined, taking into account serviceability and the life of the equipment and devices in which these products are used, and also the possibility to solve the technical problems which are solved in different ways with large expenditures and inconveniences, or they are not solved at all.

CONCLUSION

The radiation chemistry of polymers as an independent branch science has been in existence about two decades, but, despite such a short life serious results have already been achieved in this area. Along with the development of theoretical presentations about the regularities of primary transformations and the investigation of the reaction mechanisms which proceed under the action of ionizing high-energy radiation, the bases for radiochemical technology have been laid.

The realization of methods of the directed changing of the properties of polymeric materials both in the initial state and directly in the finished product opens wide possibilities not only for the chemical industry, but also for all branches of the national economy which use polymeric materials in the production of products.

The assortment of synthetic polymeric materials is continuously being expanded, however, the demands of intensively developing branches of new technology outstrip the present possibilities and in this connection radiation modification proves to be a very convenient and promising instrument for imparting a new complex of properties to materials which have already been mastered by the chemical industry.

It is not accidental that many foreign firms are actively assimilating radiochemical processes for the modification of polymers, which is testified to by the constantly growing volume of production and the assortment of products from irradiated polyolefins [564, 565].

The problems examined above were limited basically to the electrotechnical application of irradiated polymeric materials. At the same time it is evident that the use of products from

these materials is very promising even in many other areas of industry, and also in the national economy as a whole.

The fundamental problem today consists in the practical mastering of the accumulated scientific information, i.e., the working out and incorporation of radiation procedures into industry.

There is no doubt that the successful solution to this problem will facilitate further technical progress to a considerable extent.

APPENDIX

1. FUNDAMENTAL RADIOMETRIC AND DOSIMETRIC UNITS

In the examination of problems connected with radiation materials management there is fundamental importance in units for the measurement of the energy content of radiation absorbed in the irradiated system, or for the characteristic of radiation fields.

The concept of "radiation dose" [561, 562] is introduced for the characteristics of the radiation fields created by some radiation sources. The radiation dose is the measure of radiation based on the capacity of the latter to ionize the medium. The unit of radiation dose is accepted as the roentgen (r) - that dose of X-ray or γ-radiation in the air, at which conjugating corpuscular emission per 0.001293 grams of air[1] conducts in the air ions which are carrying a charge in one electrostatic unit of the quantity of electricity of each sign.

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[1]The number 0.001293 represents a mass of 1 cm^3 of atmospheric air at a temperature of 0°C and pressure of 760 mm Hg.

Today the unit of absorbed dose is used - 1 rad[1] = 100 erg/g. Thus a dose of 1×10^6 rads, or 1 Mrad, corresponds to an energy absorption of 10^8 erg/g = 2.4 Cal/g. Therefore, 1 Mrad·g is simply equal to 10 joule of absorbed energy of radiation, and one and the same radiation in different materials will create various doses expressed in rads. The radiation which imparts to water a dose of 1 rad imparts to air a dose of about 0.9 rads. Many organic materials in their absorbing capacity are sufficiently close to water and for them this difference can be neglected.

Rad - the most convenient unit for the comparison of the energy efficiency of the radiation source with the radiochemical changes produced by it in the irradiated system. Absorbed energy, in order to produce a chemical change which requires r megarad, in m grams of substance is equal to $r \cdot m \cdot 10^8$ erg, or $10r \cdot m$ joules.

One ought to emphasize that the roentgen and rad are units of the integral dose of radiation and complete quantity of energy absorbed in the system.

The dose rate is the radiation dose created by it in an unit of time at a given point of space. The unit of dose rate is usually roentgen per second (r/s) [561, 562] or megarad per second (Mrad/s).

Another important radiometric characteristic is the intensity of radiation. The intensity of γ-radiation J is determined by the energy content passing in an unit of time through a unit of surface normal to the incident direction of the rays. If through 1 cm^2 in 1 s n γ-quanta with an energy hν (MeV) pass, then the

[1]The name of the unit is formed from the first letters of the term radiation absorbed dose (English).

intensity of radiation will be [Mev/($cm^2 \cdot s$)]

$$J = nh\nu.$$

The dose rate P (r/s) is connected with intensity by the following relationship:

$$P = nh\nu \frac{1.6 \cdot 10^{-6} \sigma_a}{0,11} \approx 1,45 \times 10^{-5} nh\nu\sigma_a,$$

where 0.11 - the energy equivalent of roentgen in air, erg/$cm^3 \cdot r$; σ_α - the linear coefficient of electron conversion in air (cm^{-1}), showing which fraction of the total intensity of γ-quanta transforms into secondary electrons during passage through a layer of air with a thickness of 1 cm. The values of σ_α and its dependence on the energy of the γ-quanta are given in literature (see, for example, [563]).

The determination of the integral flux of mixed radiation, for example reactor (neutrons of a wide energy spectrum and corresponding γ-radiation) presents definite difficulties conditioned by the dependence of the absorbed dose of neutron radiation on the neutron energy, and also on the chemical composition of the irradiated medium.

Fast neutrons lose their energy, primarily as a result of collisions with the atoms of hydrogen since the masses of both particles are close and during every collision maximum energy can be transmitted. In a sample containing a large quantity of atoms of hydrogen the fast neutrons beat out the nuclei of hydrogen and therefore cause the appearance of high-energy protons generating ionization of high density inside the sample. The contribution of fast neutrons to the absorbed dose of neutron radiation depends basically on hydrogen concentration in the irradiated sample. For instance, for polyethylene $(-CH_2-CH_2-)_n$ irradiation in a reactor up to an integral dose of 10^{17} neutron/cm^2 is equivalent to the action of a dose of 45 Mrad of pure γ-radiation, whereas for polytetrafluoroethylene $(-CF_2-CF_2-)_n$, which

does not contain atoms of hydrogen, the effect is less and corresponds to only 30 Mrad of γ-radiation [14].

γ-radiation can interact directly with atomic nuclei only at a very high energy. In a nuclear reactor the main effect of γ-radiation is manifested in the formation of fast electrons with a Compton effect (the contributions of the processes of photo-electric absorption and pair formation are very small). The number of Compton electrons depends only on the number of electrons in a gram of substance; for many elements this number is proportional to the ratio of atomic number to atomic weight (Z/A). For the majority of the elements which are present in polymers (besides hydrogen) Z/A is close to 0.5. An insignificant difference in energy release occurs due to the difference in the hydrogen content which changes the electron density from 3.4×10^{23} g^{-1} in polyethylene to 2.89×10^{23} g^{-1} in polytetrafluoroethylene.

Neutron absorption leads to the onset of the so-called capture γ-radiation and to the formation of induced activity. In hydrogen, for example, slow neutrons can be absorbed, forming deuterium; in this case γ-quanta with an energy of 2.17 MeV are emitted. The effective cross section of this process is small, the energy absorption of γ-radiation is also small, therefore for small samples containing only hydrogen, carbon, and oxygen the contribution of the slow-neutron flux to integral dose is insignificant.

For such elements as chlorine, which have a large cross section of capture, the contribution of slow neutrons to the total energy release can be significant as a result of the course of nuclear reactions of the type $Cl^{35}(n, p)S^{35}$, in which Cl^{35} - an isotope, which was contained to the extent of 75% in natural chlorine, absorbs slow neutrons and emits protons, coverting into S^{35}. The protons emitted cause the intensive local ionization,

which strongly increases the total energy release in such samples. Below radiation doses (in Mrad) are noted which are equivalent to an integral flux of neutrons of 10^{18} neutron/cm^2 for polymers of different chemical structure [369].

Polymer	Dose, Mrad
Natural rubber, butyl rubber, butadiene-styrene rubber.	600
Polystyrene, polyvinyl carbazole, polymethyl methacrylate, cellulose acetate	700
Polybutadiene	800
Polyethylene, polytetrafluoroethylene, nylon, polyethylene terephthalate.	1000
Neoprene, Hypalon, polyvinyl chloride, polyvinyl chloride-acetate.	2500

For the conversion of various units used in the study of radiation materials it is convenient to use the following relationships:

$$1\ \text{eV} = 1.602 \times 10^{-12}\ \text{erg}$$
$$1\ \text{erg} = 6.24 \times 10^{-11}\ \text{ev}$$
$$1\ \text{cal} = 4.185 \times 10^{7}\ \text{erg}$$
$$1\ \text{W} = 6.24 \times 10^{13}\ \text{eV/s}$$
$$1\ \text{Cal/mole} = 0.0433\ \text{eV/molecule}$$
$$1\ \text{eV/molecule} = 23.1\ \text{Cal/mole}.$$

The energy of a quantum (in keV) = 12.40λ (λ - the wave length in Å)

$$1\ \text{Rad} = \begin{cases} 100\ \text{erg (absorbed energy)/g of substance} \\ 6.24 \times 10^{13}\ \text{erg} \\ 1.14\ \text{r (in dry air)} \\ 1.83 \times 10^{12}\ \text{pairs of ions/g of air} \\ 1 \times 10^{-5}\ \text{W·s/g} \\ 1.73 \times 10^{-9}\ \text{W·h/g} \\ 1.16 \times 10^{-10}\ \text{W·24h/g} \\ 2.39 \times 10\ \text{Cal/g} \\ 1 \times 10^{-6}\ \text{Mrad} \end{cases}$$

Below some useful, although very approximate, evaluations of relatinoships between various units of measures of dose are given.

Form of Radiation	Unit used	Equivalent, rad
Any	Mrad	10^6
X-ray and γ-radiation	Roentgen	0.93
Neutrons	Thermal neutron per 1 cm^2	10^{-9}
Neutrons	Fast neutron (2 MeV) per 1 cm^2	0.3×10^{-8}
γ-radiation	γ-quantum (2 MeV) per 1 cm^2	0.7×10^{-9}
Electrons	Electron (1 MeV) per 1 cm^2	0.4×10^{-7}

2. The Basic Characteristics of Soviet Wires and Cables with Insulation Made From Irradiated Polyolefins

1. *Wiring leads, heat resistant with insulation made from irradiated polyethylene* (TU 017-34-63).

The wires are intended for service under the variable influence of temperatures from -60 to 100°C and relative humidity up to 95 ± 3% at 40°C. Overheating to 200°C for 5 min with a total duration of no more than 30 min is allowed.

Based on design features the wires are separated into the following brands:

[MPO] (МПО) - a wire irradiated with insulation made from polyethylene:

[MPOE] (МПОЭ) - the same, screened.

The wires are made with a flexible stranded core with the following sections: 0.12; 0.2; 0.35; 0.5; 0.75; 1; 1.5; 2.5; 4; and 6 mm^2.

The resistance of insulation after a three-hour stay of the wire in water at a temperature of 20°C is no less than 50,000 MΩ·m, and after a two-hour heating at a temperature of 100°C no less than 1000 MΩ·m.

Operating voltage of up to 220 V alternating current with a frequency of up to 2000 Hz.

2. *Wiring lead, thermoradiation resistant with insalation made from irradiated heat stabilized polyethylene* (TU 017-96-65).

The wires are intended for service under the variable influence of temperatures from -60 to 150°C and relative humidity up to 95 ± 3% at 40°C, and also in radiation fields. Service life at a temperature of 150°C is no less than 1000 h. Overheating up to 200°C for a limited time is permitted.

Based on design features the wires are separated into the following brands:

MSTP - wiring leads with insulation made from glass fiber and termostabilized polyethylene, irradiated; MSTPE - the same, screened; MSTPS - the same, in covering made from glass fiber;

MSTPL - the same, in covering made from dacron; MLTP - wiring lead with insulation made from dacron and thermostabilized polyethylene, irradiated; MLTPL - the same, in a covering made from dacron. The wires are prepared with a bending stranded core with the following sections: 0.12; 0.2; 0.35; 0.5; 0.75; 1; 1.5; 2.5; 4 and 6 mm^2.

The insulation resistance after a three-hour stay of the wire in water at a temperature of 20°C is no less than 50,000 MΩ·m, the insulation resistance measured at a temperature of 150°C after a two-hour stay at that temperature, no less than 5000 MΩ·m and after a 48-hour stay under conditions of relative humidity of 98% at a temperature of 40°C no less than 1000 MΩ·m.

Operating voltage of up to 220 V alternating current with a frequency of up to 1000 Hz.

3. *Cable, thermoradiation resistant with insulation and jacket made of irradiated thermostabilized polyethylene.*

The cable is intended for service at an ambient temperature of from -60 to 150°C and relative humidity up to 98% at a temperature of 40°C.

The service life at a temperature of 150°C is no less than 1000 h. Overheating up to 200°C with a total duration of not more than 3 h is permitted. The cable can be used in neutron fluxes of up to 1×10^{12} neutron/(cm^2·s).

The cable has been awarded the brand KTR (cable thermoradiation resistant), it is made with a bending stranded core with a section of 0.5 mm^2, above the insulation of the current-conducting core a screening covering and protective jacket are applied.

The insulation resistance after a three-hour stay of the cable in water at a temperature of 20°C is no less than 50,000 m 50,000 MΩ•m; the insulation resistance measured at a temperature of 150°C after a two-hour stay at that temperature is no less than 5000 MΩ•m, and after a 48-h stay under conditions of relative humidity of 98% at a temperature of 40°C is no less than 1000 MΩ•m.

Operating voltage is 500 V direct current.

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